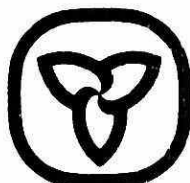


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THE USE, CHARACTERISTICS AND TOXICITY OF MINE-MILL REAGENTS IN THE PROVINCE OF ONTARIO

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Ontario

Ministry
of the
Environment

The Honourable
Keith C. Norton, Q.C.,
Minister

Gérard J. M. Raymond
Deputy Minister

THE USE, CHARACTERISTICS AND TOXICITY
OF
MINE-MILL REAGENTS
IN THE
PROVINCE OF ONTARIO

STANDARDS DEVELOPMENT BRANCH
135 ST. CLAIR AVENUE WEST
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by

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INTRODUCTION

At the present time, most modern mine-mill operations employ a variety of chemicals to achieve profitable extraction of metals and non-metals from their respective ores. The chemicals themselves tend to be relatively expensive and, as such, the mining industry attempts to use the chemicals wisely and with little waste. Even a small mining operation, however, may require several hundred pounds of essential chemicals during a normal working day. Residual quantities of many of these compounds can and do escape in effluents to receiving watercourses. Also, accidental chemical spills can and do occur. Up to the present time, the toxicity of these numerous chemicals to aquatic life and the effects of these chemicals on water quality were largely unknown or not available in a single document. It is for these reasons that this report was written.

GENERAL STATEMENT

'I Know That
You Believe You
Understand What
You Think I Said

But

I Am Not Sure
You Realize That
What You Understood
Is Not
What I Meant'

The toxicity information contained within this report is of varying degrees of reliability. Therefore, the reader is expected to check all reference sources quoted in this report.

The results of many bioassay tests run on samples of mine-mill reagents by the former Ontario Water Resources Commission laboratory (now the laboratory of the Ontario Ministry of the Environment) are given in this report. Three types of animals

(all frequently found in waters of the mining districts of Ontario) were used in the bioassay tests:

- (1) *Daphnia magna* -- a small crustacean
- (2) *Notropis atherinoides* -- emerald shiner
- (3) *Pimephales promelas* -- fathead minnow

One or more of these animals were used to establish a toxicity range for each reagent tested. The toxicity range noted for each reagent simply gives an indication of the concentration of that particular reagent that could cause problems in a receiving watercourse. In general, it is expected that the 96-hour median tolerance level (TL_m 96) for each reagent will lie somewhere within the range given for each reagent.

The toxicity information contained in this report is almost exclusively based on acute toxicity data obtained from short-term bioassay studies. These types of data, while very useful for estimating relative potencies of industrial chemicals, may be quite misleading when it comes to assessing long-term effects on the aquatic biota and constitute a very poor basis for establishing safe levels in receiving waters. Nevertheless, often as not, the data are all that are available and must be used cautiously pending the availability of more relevant bioassay results.

Many of the studies referred to in this report were performed in the early days of toxicity testing without the benefits of modern methodology. This is not to say that all the older data are inaccurate but rather to caution that some of the values quoted may not be directly comparable to more recent findings. This is essentially the explanation for the frequent occurrences of apparently conflicting groups of data in commonly-quoted toxicity literature. Many of the early authors, in addition,

failed to record the precise conditions of their testing procedures. Their results, therefore, for use at the present time, are of doubtful value.

The material contained in this report is offered to the reader solely for consideration, investigation and verification. Under no circumstances should the material contained in this report be considered sufficiently accurate to permit an individual to recommend to a company or an agency that a specific reagent be substituted for another in order to reduce the toxic impact of a particular waste stream. The toxicity data contained in this report, however, will give the reader very valuable indications of the relative toxicities of various mine-mill reagents and will indicate problems that could arise as a result of the use of individual reagents or specific groups of reagents.

SUMMARY

The intended function of this report is to give the reader a general impression of the toxicity of the mine-mill reagents that are presently available for use in the Province of Ontario. Hopefully, this report will also stimulate active and detailed research by private individuals and agencies into the toxicity and environmental effects of the compounds used by the mining industry.

The nature of this report is such that specific recommendations concerning specific reagents are not made. However, the following general conclusions are worthy of note and should be considered whenever a mine-mill circuit or process is being designed:

- (1) Mine-mill reagents vary in toxicity. Some are highly toxic while others, considering the circumstances of use, are relatively non-toxic. Some are persistent and hence will escape from a tailings area. Others are unstable and will break down in a tailings area.

Obviously, when reagents are being chosen for use in a mine-mill circuit, the least toxic compounds available should be chosen. Included in the definition of 'least' toxic compounds are those toxic compounds that break down rapidly (into innocuous substances) in a waste stream or those toxic substances which can be removed easily from a waste stream using accepted waste treatment technology.

- (2) The use of mine-mill reagents that are persistent (that is, reagents that do not break down easily in a natural environment) should be avoided if possible.
- (3) The use of mine-mill reagents having known or suspected nutrient properties should be avoided if possible.
- (4) When choosing a reagent for use in a mine-mill circuit or process, the total effect of that particular reagent on the receiving watercourse should always be considered. Reagent characteristics to investigate, for instance, would generally include chemical oxygen demand, biochemical oxygen demand, biodegradability, effects on local aquatic life (plant and animal) and effects on the total dissolved solids concentration and hardness of the receiving stream.
- (5) The use of mine-mill reagents that consist of or contain water-soluble salts of metals that are known to exhibit undesirable environmental effects should be avoided if possible.

BULK CHEMICALS

Chemicals that are used or produced in very large volumes or great quantities by the mining industry in the Province of Ontario are referred to as 'bulk' chemicals. For the purposes of this report, the term 'bulk chemicals' does not include gasoline, fuel oil, diesel oil or similar petroleum products.

Since the bulk chemicals are the most commonly used chemicals in the mining industry, these are the chemicals that most frequently gain access to and influence water quality characteristics in natural watercourses. These are the chemicals that are most frequently involved in storage tank failures and transportation accidents.

In general, the bulk chemicals finding use in the Province of Ontario can be conveniently divided into two simple categories: acids and bases. The bulk acids are sulphuric acid, nitric acid and hydrochloric acid. The bulk bases are ammonia, calcium oxide, sodium carbonate and sodium hydroxide.

In each of the following sections, a specific bulk chemical is discussed in detail. General toxicity informa-

tion is given for each substance.

(1) Name: Sulphuric Acid

Formula: H_2SO_4

Physical and Chemical Characteristics:

Sulphuric acid is a heavy oily liquid which, depending on the grade and strength, ranges from clear to cloudy in appearance. It is strongly corrosive to textiles, skin, wood and similar organic matter. Hot concentrated sulphuric acid dissolves most metals with the evolution of sulphur dioxide but at concentrations above 77 percent (60°Bé) and at ordinary temperatures it has little effect on mild steel and cast iron. At lower concentrations, it rapidly attacks these metals with the formation of hydrogen, but does not affect lead. Sulphuric acid has a strong affinity for water with which it is completely miscible, resulting in the evolution of heat and a marked volume reduction.

Many organic substances such as wood, sugar, starch, etc., are strongly dehydrated on contact with concentrated sulphuric acid, forming carbon. Very small quantities of organic matter are sufficient to blacken concentrated sulphuric acid, the discolouration being caused by

suspended carbon.

Electrolytic grade sulphuric acid has a higher purity than regular commercial acid.

Sulphuric Acid

	<u>Electrolytic</u>	<u>66° Be'</u>	98%/99%
Strength as H_2SO_4	93.0 to 93.6%	93.2% (min.)	98 to 99.2%
Degrees Baume	66°	66°	--
Specific Gravity at 60°F/ 60°F	1.8354	1.8354	1.8437 to 1.8418
Pounds Per Imperial Gallon at 60°F	18.35	18.35	18.44 to 18.42
Pounds Per Cubic Foot at 60°F	114.47	114.47	114.99 to 114.87
Freezing Point (approximate)	-22° to -36.4°F	-22° to -34°F	34° to 45°F

Hazards of Handling Sulphuric Acid:

Sulphuric acid is dangerous when handled improperly. It will rapidly destroy clothing and, in general, char wood

and organic material. Concentrated solutions are rapidly destructive to skin tissues, producing severe burns. Contact with the eyes can cause serious damage and may result in total loss of sight. Swallowing sulphuric acid or inhalation of concentrated vapour from hot acid will result in severe injury to the internal organs or upper respiratory tract.

Sulphuric acid itself is not flammable but the concentrated acid may cause ignition of combustible materials. It should, therefore, be isolated from organic materials and from such products as nitrates, carbides, chlorates and metallic powders.

A highly flammable gas, hydrogen, is generated by the action of sulphuric acid on iron or steel. Although in the case of concentrated acid the amount formed is small, an explosion may result if open lights or flames are allowed near open storage tanks, containers, vents and pipe lines.

Heat is evolved when sulphuric acid and water are mixed. Addition of water to concentrated acid gives rise to violent local heating and may result in boiling and splashing of the solution.

Uses of Sulphuric Acid in the Mining Industry:

(a) In the uranium-producing Elliot Lake district of Ontario, great quantities of sulphuric acid are used to leach uranium values from the ore. In this mining camp, mill capacities range from 3,000 to 6,000 tons of ore per day. During treatment, each ton of ore consumes approximately 65 to 70 pounds of 100 percent sulphuric acid.

(b) Sulphuric acid is not commonly used in the flotation of sulphide ores. However, there are a few operations in which the entire ore in a circuit is acidified with sulphuric acid; or portions--specifically slime portions--of copper ores in a circuit are acidified with sulphuric acid.

In some operations, sulphuric acid is employed in the production of an iron sulphide concentrate. This is usually done after other sulphide minerals have been floated and the iron sulphides have been depressed in alkaline circuits.

The use of sulphuric acid in the flotation of certain non-metallic and metallic oxide ores is increasing.

Toxicity of Sulphuric Acid:

The following concentrations of sulphuric acid in

water have been reported as lethal or toxic towards fish:

<u>Concentration of H₂SO₄ in mg/litre</u>	<u>Time of Exposure</u>	<u>Type of Water</u>	<u>Species of Fish</u>	<u>Reference</u>
1.2	--	--	Sunfish	a
6.0 to 8.0	6 hours	Distilled 20°C	Minnows	b
6.25	24 hours	--	Trout	c
7.36	60 hours	Distilled	Bluegills	d
10.0	--	--	Gamefish	e
24.5	24 hours	--	Bluegills	f
26.0	15 minutes	Tap	Minnows	g
42	96-hour TL _m	Turbid	Mosquito- fish	h
49	48-hour TL _m	Tap, 20°C	Bluegill sunfish	i
59.0	1 to 1.25 hours	Soft, pH 3.2	Goldfish	j
71.2	--	--	Pickrel	k
80.1	--	--	Whitefish	l
110 to 120	6 hours	Hard, 20°C	Minnows	m
138	4 hours	Hard, pH 4	Goldfish	n
167	48 hours	--	Fish	o

- (a) Belding, D.L., "Toxicity Experiments with Fish in Reference to Trade Waste Pollution", Trans. Amer. Fish. Soc. (1927).
 - (b) Le Clerc, E., "The Self-Purification of Streams and the Relationship Between Chemical and Biological Tests", Proc. of the 2nd Symposium on the Treatment of Waste Waters, Pergamon Press, London (1960).
 - (c) See (a) above.
 - (d) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
 - (e) Anon., "Ministry of Agriculture and Fisheries, Salmon and Freshwater Fisheries Report for the Year 1937", Water Pollution Abs. (March 1939).
- Reid, K.A., "Pollution of Streams from Mining Operations", No. American Wildlife Conference I, 544 to 550 (1936).
- (f) See (a) above.
 - (g) Schaut, G.G., "Fish Catastrophes During Drought", Jour. A.W.W.A. (1939).
 - (h) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to Gambusia affinis of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
 - (i) Turnbull, H., DeMann, J.G., and Weston, R.F., "Toxicity of Various Refinery Materials to Fresh Water Fish", Symposium on Waste Disposal in the Petroleum Industry, Ind. Eng. Chem. (1954).
 - (j) See (d) above.
 - (k) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee", Report No. 3 (1950).

- (l) See (k) above.
- (m) See (b) above.
- (n) See (d) above.
- (o) Laurent, P., "Toxicity Tests with Fish", Bull. Franc. Piscic (1954); Water Pollution Abs. (1955).

Towards other aquatic life, the following concentrations of sulphuric acid were reported as harmful:

<u>Concentration of H₂SO₄ in mg/litre</u>	<u>Time of Exposure</u>	<u>Type of Water</u>	<u>Species of Fish</u>	<u>Reference</u>
29	24 to 72 hours	Soft, pH 5	Daphnia Magna	p
33.11	--	--	Bivalve Larvae	α
50	--	--	All aquatic life	r
88	64 hours	Lake Erie	Daphnia Magna	s
138	--	--	Daphnia Magna	t

- (p) See (d) above.
- (α) Woelke, C.E., "Bioassay - The Bivalve Larvae Tool", Proc. of the 10th Northwest Symposium on Water Pollution Research, "Toxicity in the Aquatic Environment", Portland Ore. (1961).
- (r) See (e) above, second reference.

- (s) Anderson, B.G., "The Toxicity Thresholds of Various Substances Found in Industrial Wastes as Determined by the Use of Daphnia Magna", Sewage Works Jour. (1944).
- (t) See (k) above

Environmental Effects of Sulphuric Acid:

Sulphuric acid dissociates almost completely in water to release sulphate ions and hydrogen ions. A pH depression results.

At very low pH values (3.0 and lower), some of the sulphate ion will remain as acid sulphate HSO_4^- but at higher pH values dissociation to sulphate ions is practically complete.

If sulphuric acid gains access to a watercourse, the following problems in the watercourse can be anticipated :

- (i) a pH depression
- (ii) an increase in sulphate concentration
- (iii) an increase in total dissolved solids concentration

The toxicity of sulphuric acid towards aquatic life is a function of the resulting pH. A dose that would be lethal in distilled or soft water might be harmless in a highly buffered water. Strong mineral acids, such as sulphuric acid, apparently can be directly lethal to fully

developed fish in most natural waters only when the pH is reduced to 5.0 or lower. Death of trout has been reported at pH 3.9 while for sunfish, bass and carp a pH of 3.5 caused death and 4.0 gave pronounced gill irritation.

(2) Name: Nitric Acid

Formula: HNO_3

Physical and Chemical Characteristics:

Pure (100 percent) nitric acid is a clear, colourless liquid that is very hygroscopic and is miscible with water in all proportions. Commercial acid, an acid-water mixture, generally contains approximately 60 percent to 68 percent nitric acid and exhibits a specific gravity of 1.41. Nitric acid is noncombustible but is dangerously reactive with many materials. It can react explosively with metallic powders, carbides, hydrogen sulphide and turpentine. It increases the flammability of combustible, organic and readily oxidizable materials and, under favourable circumstances, can cause ignition of some of these materials.

Hazards of Handling Nitric Acid:

Nitric acid fumes are toxic. The acid itself causes severe tissue burns.

Uses of Nitric Acid in the Mining Industry:

Nitric acid finds use, on a low volume basis, in a few mine-mill circuits in the Province of Ontario. Its greatest use, however, seems to be centered in the uranium producing Elliot Lake camp. Here, nitric acid consumption approximates 4 pounds per ton of ore milled.

Toxicity of Nitric Acid:

The following concentrations of nitric acid have been cited as toxic or lethal to fish:

<u>Concentration in mg/litre</u>	<u>Result- ing pH</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Refer- ence</u>
1.6	--	--	--	Trout	a
1.6 to 20	--	--	--	Fish	b
15.6	--	--	24 hours	Trout	c
72	6.2	Turbid	96 hour TL _m	Mosquito- fish	d
98.5	--	--	--	Pickrel	e
113	--	--	--	Whitefish	f
200	--	--	--	Minnows, Goldfish	g
750	3.4	Hard	½ to 1 hour	Goldfish	h
1,000	--	Tap	½ hour	Trout	i
1,000	4.4	--	7 hours	Minnows	j

- (a) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee", Report No. 3 (1950).
- (b) Belding, D.L., "Toxicity Experiments With Fish in Reference to Trade Waste Pollution", Trans. Amer. Fish. Soc. (1927).
- (c) See (b) above.
- (d) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to Gambusia affinis of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (e) See (a) above.
- (f) See (a) above.
- (g) See (b) above.
- (h) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).

Also see (a) above.
- (i) See (h) above (first reference).
- (j) See (h) above (first reference).

In contrast, the following concentrations of nitric acid have not been harmful to fish within the time specified:

<u>Concentration in mg/litre</u>	<u>Resulting pH</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
5.75	5.2	--	Minnows	k
5.75	--	--	Shiners	l
5.75 to 20	--	--	Fish	m
20	--	--	Carp, Gold- fish, Suckers	n
200	--	Greater than 100 hours	Goldfish	o
200	4.9	Greater than 4 days	Goldfish	p

(k) See (h) above (first reference).

(l) See (b) above.

(m) See (b) above.

(n) See (b) above.

(o) See (h) above (first reference).

(p) Phelps, E.B., "Stream Sanitation", John Wiley and Sons (1944).

Environmental Effects of Nitric Acid:

Nitric acid (as well as other strong acids) appears to be directly lethal to fully developed fish only when it reduces the pH to 5.0 or less. Nitric acid in water dissociates

completely into hydrogen ions and nitrate ions with a resulting tendency to lower the pH value. Its principal deleterious effect, therefore, is its acid reaction.

In the following paper:

Rudolf, 2., "Principles of the Determination of the Physical and Chemical Standards of Water for Drinking, Industrial, and Domestic Purposes", GAZ:Woda (1930); Water Pollution Abs. (March 1931)

it is reported that free nitric acid and nitrates in concentrations of 15 to 30 mg/litre render water harmful or dangerous for domestic, drinking and industrial purposes.

If nitric acid gains access to a watercourse, the following problems in the watercourse can be anticipated :

- (i) a pH depression
 - (ii) an increase in nitrate concentration
 - (iii) an increase in total dissolved solids concentration
 - (iv) a possible nutrient problem
- (3) Name: Hydrochloric Acid

Formula: HCl

Physical and Chemical Characteristics:

Hydrochloric acid is a strongly corrosive solution (HCl and water) which in higher concentrations gives rise to the strong pungent odour of hydrogen chloride and strongly

fumes in moist air. The pure solution is colourless but traces of iron, chlorine or organic matter impart a yellow tinge. Highly soluble in water, concentrated hydrochloric acid is one of the strongest acids known. It readily attacks all of the common metals to yield hydrogen which, in certain concentrations in air, may be highly explosive.

Boiling Point HCl - 110°C (230°F)

Specific gravity HCl - 1.01 to 1.21 (values change with concentration)

Hazards of Handling Hydrochloric Acid:

Hydrochloric acid is capable of causing severe flesh burns and its vapours are irritating to the skin, eyes and mucous membranes. Inhalation of concentrations of HCl of about 1,500 parts per million in air are fatal in a few minutes.

Uses of Hydrochloric Acid in the Mining Industry:

At the present time, hydrochloric acid finds only limited use in the mine-mill circuits in the Province of Ontario. However, future large volume use by the industry is probable. A number of processes are known, for instance, in which iron, cobalt, nickel, vanadium, molybdenum and phosphates can be recovered from their respective ores via a hydrochloric

acid route.

Toxicity of Hydrochloric Acid:

The following concentrations of hydrochloric acid in water have been reported as lethal or toxic towards fish:

<u>Concentration of HCl in mg/litre</u>	<u>Time of Exposure</u>	<u>Species of Fish</u>	<u>Remarks</u>	<u>Reference</u>
3.6	48 hours	Sunfish	Lethal in dis- tilled water	a
3.65	24 hours	Carp, Shiners, Suckers	Lethal	b
4 to 6	6 hours	Minnows	Minimum lethal concentration in distilled water	c
8.0	24 hours	Sunfish	Lethal	d
10	24 hours	Trout	Minimum lethal concentration	e
67.5	--	White- fish, Pickerel	Toxic threshold	f
80	24 hours	Creek Chub	Lethal	g
100 to 110	6 hours	Minnows	Minimum lethal concentration in hard water	h
166	4 to 7 hours	Goldfish	Killed in hard water	i

<u>Concentration of HCl in mg/litre</u>	<u>Time of Exposure</u>	<u>Species of Fish</u>	<u>Remarks</u>	<u>Reference</u>
200	--	Perch, Roach	Collapsed in distilled water	j
282	96-hour TL _m	Mosquito fish	Turbid water	k
1,000	2 to 5 minutes	Trout	Overtured in tap water	l

- (a) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (b) Belding, D.L., "Toxicity Experiments with Fish in Reference to Trade Waste Pollution", Trans. Amer. Fish. Soc. (1927).
- (c) Le Clerc, E., "The Self-Purification of Streams and the Relationship Between Chemical and Biological Tests", Proc. of the 2nd Symposium on the Treatment of Waste Waters, Pergamon Press, London (1960).
- (d) See (b) above.
- (e) See (b) above.
- (f) See (b) above.
- (g) Gillette, L.A., Miller, D.L., and Redman, H.E., "Appraisal of a Chemical Waste Problem by Fish Toxicity Test", Sewage and Industrial Wastes (1952).
- (h) See (c) above.
- (i) See (a) above.
- (j) See (a) above.

- (k) Wallen, I.E., Greer, W.C., and Lasater R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (l) See (a) above.

Environmental Effects of HCl:

Hydrochloric acid is highly soluble in water and dissociates into hydrogen and chloride ions. Inasmuch as the chloride ions are relatively innocuous, the principal effect of HCl lies in changing the hydrogen-ion concentration (pH) except in highly buffered waters. Only when the pH is depressed to 5.0 or lower will HCl prove lethal to fish. For instance, the 96-hour TL_m at 20°C for the bluegill sunfish occurs when the pH value is lowered to 3.6 by HCl. Corresponding lethal pH values of 4.0 and 4.6 have been reported for goldfish and sticklebacks, respectively. At pH 5.0, sticklebacks have survived for 9 days in water to which HCl had been added; at pH 4.0, only 10.5 hours; and at pH 3.0, only 80 minutes.

Data presented concerning the environmental effects of HCl may be confusing since it is the resulting pH rather than the concentration of HCl that governs lethality towards aquatic life.

If hydrochloric acid gains access to a watercourse,

the following problems in the watercourse can be anticipated:

- (i) a pH depression
 - (ii) an increase in chloride concentration
 - (iii) an increase in total dissolved solids concentration
- (4) Name: Calcium Hydroxide (Slaked Lime)

Calcium Oxide (Quicklime)

Formula: $\text{Ca}(\text{OH})_2$ (Calcium Hydroxide)

CaO (Calcium Oxide)

Physical and Chemical Characteristics:

Solubility of $\text{Ca}(\text{OH})_2$ in CO_2 Free Water

70°F -- 1.20 grams/litre -- 10.0 lbs./1,000 gal.

175°F -- 0.67 grams/litre -- 5.6 lbs./1,000 gal.

pH of Calcium Hydroxide Solutions at 25°C

CaO

gm/litre

pH

0.064	11.27
0.065	11.28
0.122	11.54
0.164	11.66
0.271	11.89
0.462	12.10
0.680	12.29
0.710	12.31
0.975	12.44
1.027	12.47
1.160	12.53

Since the solubility of lime decreases as the temperature increases, the pH of lime solutions is correspondingly lower at higher temperatures.

Lime (CaO), a white or greyish-white solid, is available to the mining industry in the following forms: lump, crushed, pebble, pelletized, ground, granular and pulverized. Lime is not combustible but contact with water or moisture may generate sufficient heat to ignite combustible materials. Lime swells when moist and may burst containers.

Hazards of Handling Calcium Oxide:

Calcium oxide is a caustic irritant to eyes and the respiratory tract. In the presence of moisture, calcium oxide can cause skin burns.

Uses of Lime in the Mining Industry:

Lime in its various forms, as quicklime (CaO) and hydrated lime ($\text{Ca}(\text{OH})_2$), is the principal alkali used by the mining industry in Ontario. It is used in mine-mill operations and in waste treatment systems.

Lime is the most commonly used alkalinity or pH regulator. It is generally used in flotation operations in the form of slaked lime ($\text{Ca}(\text{OH})_2$). The quantity of lime

required in any operation varies considerably depending on the pH desired and the extent to which naturally occurring lime-consuming constituents are present in the ore.

Lime usually has a flocculating effect on ore slimes while sodium carbonate tends to act as a dispersant for such slimes. Lime is cheaper than sodium carbonate in most areas and for this reason is widely used for the treatment of sulphide ores; particularly those of copper and zinc. Generally, sodium carbonate is preferred for the treatment of lead sulphide ores and precious metal ores; lime tends to depress galena and metallic gold and needs much more careful control in its addition than does sodium carbonate.

In addition to being an alkalinity regulator, lime is a depressant for the iron sulphides (pyrite, pyrrhotite and marcasite) and for arsenopyrite and cobalt and nickel sulphides. In this application, it is often used with cyanide.

Toxicity of Calcium Hydroxide:

The following concentrations of calcium hydroxide have been reported as toxic to fish in the time specified:

<u>Concentration in mg/litre</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
18	--	Fish	a
92	26 minutes	Trout	b
< 100 (pH 11.1)	--	Goldfish	c
100	3 to 5 hours	Goldfish, Bass, Sunfish	d
100 (unadjusted pH)	3 to 7 days	Bass	e
100 to 200	--	Carp	f
198	10 minutes	Trout	g
200 (unadjusted pH)	30 to 80 minutes	Goldfish, Bass	h
500 (unadjusted pH)	20 to 53 minutes	Goldfish	i
700	26 minutes	Trout	j

- (a) Moore, E., "Stream Pollution as it Affects Fish Life", Sewage Works Jour. (1932).
- (b) Meinck, F., Stoof, H., and Kohlschutter, H., "Industrial Waste Waters (Industrie-Abwasser)", 2nd Edition., Gustav Fischer Verlag. Stuttgart (1956).
- (c) Jones, J.R.E., "Fish and River Pollution", Chapter 7 of "Aspects of River Pollution", L. Klein, Editor, Butterworth Scientific Publ. London (1957).

- (d) Keller, E.L., Simmonds, F.A., and Baird, P.K., "Some Observations on the Effect of Alum on Certain Sheet Properties of Paper", Paper Trade Jour. (1941); Water Poll. Abs. (February 1941).
- (e) See (d) above.
- (f) Dyk, V., "The Limit of Harmfulness of Calcium Hydroxide for the Carp", Ann. Acad. Tchechosl. Agr. (1943); Water Poll. Abs. (May 1948).
- (g) See (b) above.
- (h) See (d) above.
- (i) See (d) above.
- (j) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).

Goldfish, bass and sunfish have survived 50 mg Ca(OH)_2 /litre for seven or more days (k). Using highly turbid water at 21°C to 23°C and the mosquito-fish (*Gambusia affinis*) as the test organism (l), the 24-hour, 48-hour and 96-hour TL_m values were found to be 240, 220 and 150 mg/litre of calcium hydroxide respectively.

- (k) See (d) above.
- (l) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).

Environmental Effects of Calcium Hydroxide:

If calcium hydroxide gains access to a watercourse, the following problems in the watercourse may be anticipated:

- (i) an increase in pH
- (ii) an increase in calcium concentration
- (iii) an increase in total dissolved solids concentration

(5) Name: Ammonia

Ammonium Hydroxide

Formula: NH_3 (Ammonia)

NH_4OH (Ammonium Hydroxide)

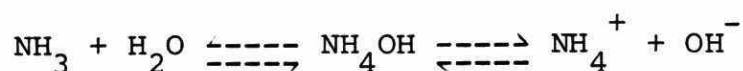
(A) Ammonia

General

In the pure form, ammonia is a colourless gas with a very pungent odour. In natural surface or ground waters, it generally results from the decomposition of nitrogenous organic matter, being one of the constituents of the complex nitrogen cycle. Rivers known to be unpolluted have very low ammonia concentrations, generally less than 0.2 mg/litre as N.

Being soluble in water to the extent of 100,000 mg/litre at 20°C, ammonia gas reacts with water, liberating much heat, to form ammonium hydroxide. This, in turn, dis-

sociates readily into ammonium and hydroxyl ions, thereby tending to raise the pH value of the solution. The combined reversible equations are as follows:



Inasmuch as the dissociation constant for ammonium hydroxide is 1.8×10^{-5} at 25°C , the ratio of ammonium ions to ammonium hydroxide molecules is a function of pH as follows:

$$\frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = \frac{1.8 \times 10^{-5}}{[\text{OH}^-]}$$

At pH 6, this ratio is 1,800 to 1, at pH 7 it is 180 to 1 and at pH 8 it is 18 to 1. For common ranges of pH, therefore, it is evident that most of the ammonia in water exists in the form of ammonium ions. Furthermore, all of the common ammonium salts are also readily soluble in water, yielding NH_4^+ and an anion. In the case of the chloride, nitrate, and sulphate, the solution of ammonium salt results in a decrease in pH since part of the ammonium ions combine with hydroxyl ions in the water.

Despite the fact that the ammonium ion predominates, except at high pH values, the data in much of the literature

are in terms of ammonia (NH_3). In recent work, however, the term "ammonia nitrogen" (expressed as N) is gaining prominence. The test for ammonia nitrogen, as outlined in Standard Methods for the Analysis of Water and Sewage, measures all of the nitrogen in the form of NH_3 , NH_4OH and NH_4^+ .

Hazards of Handling Ammonia:

Ammonia is a flammable gas. The presence of oil or other combustible materials increases the fire hazard. Ammonia, in the form of a liquid or a gas, is a strong irritant and is severely corrosive to respiratory and other body tissue. Contact with ammonia in the liquid form will result in severe frostbite.

Uses of Ammonia in the Mining Industry:

At the present time, ammonia and ammonium-based compounds find wide use in the mining industry in Ontario.

Uranium processors in the Elliot Lake camp use significant quantities of ammonia to achieve a degree of pH control and to recover uranium values in the form of ammonium salts. Mills are known that utilize two tons of liquid ammonia per day. Ammonia is also used in some sulphide flotation operations for pH control. Nearly all mine-mill

operations in the Province utilize ammonium-based compounds for one reason or another (explosives are commonly ammonium-based compounds).

Toxicity of Ammonia:

According to many references, the toxicity of ammonia and ammonium salts to aquatic animals is directly related to the amount of undissociated ammonium hydroxide in the solution, which in turn is a function of pH as explained under "General" above. Thus, a high concentration of ammonium ions in water at a low pH may not be toxic, but if the pH is raised, toxicity will probably increase. It has been found that the toxicity of a given concentration of ammonium compounds toward fish increased by 200 percent or more between pH 7.4 and 8.0.

The presence of carbon dioxide, up to concentrations in the range of 15 to 60 mg/litre, appears to reduce the toxicity of ammonia presumably by lowering the pH value. Inasmuch as CO_2 is excreted by a fish via the gills, the pH value at the gill surface will be lower than in the bulk of the solution, thereby reducing the proportion of un-ionized ammonia at the gill.

The toxicity of ammonia to fish is increased markedly at low tensions of dissolved oxygen. The concentration of excreted carbon dioxide at the gill surface varies with the oxygen content of the water; hence, as the oxygen tension is reduced, the concentration of excreted CO_2 is also reduced and the pH value of the water in contact with the gill surface rises, leading to an increased toxicity of an ammonia solution.

The following concentrations of ammonia have been reported to be toxic or lethal to fish in the time specified:

<u>Concentration of NH_3 in mg/litre</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
0.3 to 0.4	--	Trout fry	a
0.3 to 1.0	--	Fish	b
0.6	100 to 200 minutes	Rainbow trout	c
0.7	390 minutes	Rainbow trout	d
1.0 to 2.0	--	Fish	e
1.2	193 minutes	Squalius cephalus	f
2.0	--	Fish	g
2.0 to 2.5	1 to 4 days	Goldfish	h
2.5	1 to 4 days	Goldfish	i
2.0 to 7	--	Fish	j
2.9	13 hours	Cichla ocellaris	k

<u>Concentration of NH₃ in mg/litre</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
3.1 (soft water 30°C)	96-hour TL _m	Bluegill sunfish	l
3.4 (soft water 20°C)	96-hour TL _m	Bluegill sunfish	m
5.0	--	Rainbow trout	n
5 to 7 (distilled water 20°C)	6 hours	Minnows	o
6 to 7 (hard water 20°C)	6 hours	Minnows	p
7 to 8	1 hour	Sunfish	q
13	--	Fish	r
17.1	1 hour	Minnows	s
23.7 (hard water 30°C)	96-hour TL _m	Bluegill sunfish	u
24.4 (hard water 20°C)	96-hour TL _m	Bluegill sunfish	v
75.7	less than 4 minutes	Trout	w

- (a) Pearson, E.A., (Editor), "Waste Disposal in Marine Environment", Pergamon Press, N.Y. (1960).
- (b) Brockway, D.R., "Metabolic Products and Their Effects", Prog. Fish Culturist (1950).
- (c) Anon., "Report of the Water Pollution Research Board, With the Report of the Director of the Water Pollution Research Laboratory for the year 1960", Dept. of Scientific and Ind. Res., H.M. Stationery Office, London (1961).

- (d) Wuhrmann, K., and Woker, H., "Contributions to the Toxicology of Fish II. Experimental Investigations of Ammonia and Hydrocyanic Acid Poisoning", Schweiz. A. Hydrol. (1948).
- (e) See (a) above.
- (f) See (d) above.
- (g) Coburn, S.E., "Forum on Industrial Waste Problems", Sewage and Industrial Wastes (1950).
- (h) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (i) Rudolfs, W., et al., "Industrial Wastes", Reinhold Publ. Co., N.Y. (1953).
- (j) Murdock, H.R., "Industrial Wastes. Some Data on Toxicity of Metals in Wastes to Fish Life are Presented", Ind. Eng. Chem. (1953).
- (k) Bastos, J.A.M., "Importance of Ammonia as an Ichthyotoxic Substance", Serv. Pisciculture Pub. (Brazil), (1954); Chem. Abs. (1955).
- (l) Anon., "The Sensitivity of Aquatic Life to Certain Chemicals Commonly Found in Industrial Wastes", Acad. of Natural Sciences, Philadelphia (1960).
- (m) See (l) above.
- (n) Meinck, F., Stooff, H., and Kohlschutter, H., "Industrial Waste Waters (Industrie-Abwasser)", 2nd Edit., Gustav. Fischer Verlag. Stuttgart (1956).
- (o) Le Clerc, E., "The Self-Purification of Streams and the Relationship between Chemical and Biological Tests", Proc. of the 2nd Symp. on the Treatment of Wastewaters. Pergamon Press, London (1960).

- (p) See (o) above.
- (q) Shelford, V.E., "An Experimental Study of the Effects of Gas Waste Upon Fishes, With Especial Reference to Stream Pollution", Bull. Ill. State Lab. Nat. Hist. (1917).
- (r) Southgate, B.A., "Treatment Disposal of Industrial Waste Waters", Dept. of Scientific and Ind. Res., H.M. Stationery Office, London (1948).
- (s) Schaut, G.G., "Fish Catastrophes During Drought", Jour. A.W.W.A. (1939).
- (u) See (l) above.
- (v) See (l) above.
- (w) Corti, U.A., "Fish and Nitrogen Compounds. The 'Matrix' of Fish, XI", Congr. Int. Limnol. (1950-1951).

It has been stated that an ammonia concentration of 1.0 mg/litre (in a watercourse) decreases the ability of hemoglobin to combine with oxygen and hence a fish may suffocate. A concentration as low as 0.3 mg/litre causes a noticeable drop in the oxygen content of the blood of fishes.

Solutions containing mixtures of ammonium and cyanide ions are more toxic to fish than solutions containing either ion alone.

With respect to aquatic life, the following results

were reported by the Academy of Natural Sciences of Philadelphia:

<u>Organism</u>	<u>Time of Exposure</u>	<u>Type of Water</u>	<u>Temperature °C</u>	<u>Concentration of NH₃ as N in mg/litre producing noted effect</u>	
Physa heterostropha (snail)	96-hour	soft	20	90	(a)
		hard	20	133.9	(a)
		soft	30	94.5	(a)
		hard	30	133.9	(a)
		soft	22	420	(b)
		hard	22	420	(b)
Navicula seminulum (diatom)	5-day	soft	28	320	(b)
		hard	28	420	(b)
		soft	30	410	(b)
		hard	30	350	(b)
		soft	22	420	(b)
		hard	22	420	(b)

(a) 96-hour TL_m

(b) 50-percent reduction in division (growth)

Algae, which thrive on high nitrate concentrations, appear to be harmed or inhibited when the nitrogen is in the form of ammonia.

(B) Ammonium Hydroxide

Ammonium hydroxide is dealt with separately from ammonia and the ammonium salts only because some references

report data in terms of ammonium hydroxide. Whenever ammonia gas or ammonium salts are dissolved in water, or when ammonium ion is formed in the decomposition of organic matter, the undissociated compound NH_4OH results. The proportion of ammonium ion and undissociated base is a function of pH and the toxicity of the resulting solution depends primarily on the concentration of NH_4OH , i.e., the undissociated compound is the toxic principle.

Inasmuch as toxicity varies considerably with pH and hence is a function of the buffering action of the water used, it is difficult to compare the results of many investigators.

Toxic concentrations of ammonium hydroxide toward fish have been reported as follows:

<u>Concentration of NH_4OH in mg/ litre</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Remarks</u>	<u>Reference</u>
4.5	--	Goldfish	Lethal	a
6.25	24 hours	Brook trout	Lethal	b
10	--	Suckers, Shiners, Carp, Trout	Lethal	c

<u>Concentration of NH₄OH in mg/ litre</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Remarks</u>	<u>Reference</u>
10	24 hours	Creek chub	Not lethal	d
13	24 hours	Suckers, Shiners, Carp	Lethal	e
15	48-hour TL _m	Bluegill sunfish	Philadelphia tap water, 20°C	f
17.5	48-hour TL _m	Fathead minnows	--	g
18.5	48-hour TL _m	Bluegill sunfish	Philadelphia tap water, regxygenated, 20°C	h
20	15 minutes	Suckers, Shiners, Carp	Lethal	i
30	24 hours	Small fish	Lethal	j
30	24 hours	Creek chub, Perch	Lethal, 15 to 21°C	k
30	--	Perch	Lethal	l
37	96-hour TL _m	Mosquito- fish	Turbid water	m

- (a) Jones, J.R.E., "Fish and River Pollution", Chapter 7 of "Aspects of River Pollution", L. Klein, Editor, Butterworth Scientific Publ., London (1957).

- (b) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- Belding, D.L., "Toxicity Experiments with Fish in Reference to Trade Waste Pollution", Trans. Amer. Fish. Soc. (1927).
- (c) Moore, E., "Stream Pollution as it Affects Fish Life", Sewage Works Jour. (1932).
- (d) Gillette, L.A., Miller, D.L., and Redman, H.E., "Appraisal of a Chemical Waste Problem by Fish Toxicity Test", Sewage and Industrial Wastes (1952).
- (e) See (b) above (both references).
- (f) Turnbull, H., DeMann, J.G., and Weston, R.F., "Toxicity of Various Refinery Materials to Fresh Water Fish", Symp. on Waste Disposal in the Petroleum Industry, Ind. Eng. Chem. (1954).
- (g) Black, H.H., McDermott, G.N., Henderson, C., Moore, W.A., and Pahren, H.R., "Industrial Waste Guide, By-Product Coke", Proc. 11th Industrial Waste Conf., Purdue University (1957).
- (h) See (f) above.
- (i) See (b) above (first reference).
- (j) See (b) above (both references).
- (k) See (d) above.
- (l) See (a) above.
- (m) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).

In contrast, it has been reported (n) that a con-

centration of 9.4 mg/litre has not harmed suckers, shiners and carp in 24 hours of exposure.

According to Anderson (o), the threshold concentration of ammonium hydroxide for the immobilization of *Daphnia magna* in Lake Erie water at 25°C was found to be less than 8.75 mg/litre.

(n) See (b) above (second reference).

(o) Anderson, B.G., "The Toxicity Threshold of Various Substances Found in Industrial Wastes as Determined by the Use of *Daphnia magna*", Sewage Works Journal (1944).

(6) Name: Sodium Carbonate (Also known as Soda Ash)

Formula: Na_2CO_3

Physical and Chemical Characteristics:

Molecular Weight	105.989
Density	2.533 gm/cc at 25°C
Melting Point	854°C (1587°F)
Specific Heat	26.41 cal/mol/°C or 0.249 cal/gm/°C
Heat of Fusion	8 K-cal/mole, or 75.5 cal/gm, or 136 Btu/lb
Stability in Air	Slowly absorbs moisture and carbon dioxide to form trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$)

Sodium carbonate is generally available as a white anhydrous powdered or granular material containing well above 99 percent Na_2CO_3 .

Sodium carbonate is readily soluble in water and has the unusual property of reaching maximum solubility at the relatively low temperature of 35.4°C (95.7°F). At this temperature, 100 parts of water will dissolve 49.7 parts of Na_2CO_3 to give a solution containing 33.2 percent by weight of Na_2CO_3 .

Uses of Sodium Carbonate in the Mining Industry:

Sodium carbonate is one of the chemicals most commonly used by the mining industry for alkalinity control in flotation operations. In general, it is employed where calcium is detrimental and lime cannot be used. Specifically, it finds application in lead flotation and with such non-metallic minerals as barite, fluorite, calcite, hematite, and scheelite.

Where gangue slimes are a particularly serious problem, sodium carbonate can be very effective in improving both grade of concentrate and recovery. Since sodium carbonate has a dispersing action, difficulty is experienced at times

in thickening and filtering flotation concentrates and tailings from sodium carbonate circuits. This can be overcome, however, by adding a flocculating agent to the pulp before it enters the thickener.

Sodium carbonate assists the flotation of arsenopyrite and, therefore, can be a useful addition agent where a non-selective bulk sulphide mineral float is desired.

Toxicity of Sodium Carbonate:

The following concentrations of sodium carbonate have been reported to kill fish:

<u>Concentration in mg/litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
68	Tap	120 hours	King salmon	a
70	Tap	120 hours	Silver salmon	b
80	Tap	120 hours	Cutthroat trout	c
200	--	4.5 hours	Bass	d
250	--	120 hours	Shiners	e
250 to 300	Tap	Few hours	Shiners, Suckers, Carp	f
300	Standard	96-hour TL _m	Sunfish	g
500	--	4.5 to 11 hours	Sunfish	h
500	--	7 to 9 hours	Bass	i

<u>Concentration in mg/litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
500	--	½ to 3 days	Bass	j
530	Tap	3 days	Bluegills	k
740	Turbid	24-hour TL _m	Mosquito-fish	l
840	Turbid	48-hour TL _m	Mosquito-fish	m
1200	Turbid	96-hour TL _m	Mosquito-fish	n

- (a) Dimick, R.E., "The Effects of Kraft Mill Waste Liquors and Some of Their Components on Certain Salmonoid Fishes of the Pacific Northwest", National Council for Stream Improvement, Tech. Bull. (1952).
- (b) See (a) above.
- (c) See (a) above.
- (d) Keller, E.C., Simmonds, F.A., and Baird, P.K., "Some Properties of Paper", Paper Trade Jour. (1941); Water Pollution Abs. (1941).
- (e) Van Horn, W.M., Anderson, J.B., and Katz, M., "The Effect of Kraft Pulp Mill Wastes on Some Aquatic Organisms", Trans. American Fisheries Soc. (1949).
- (f) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (g) Cairns, J. Jr., and Scheier, A., "The Relationship of Bluegill Sunfish Body Size to Tolerance for Some Common Chemicals", Proc. 13th Industrial Waste Conference, Purdue Univ., Engineering Bull. (1959).
- (h) See (d) above.

- (i) See (d) above.
- (j) See (d) above.
- (k) See (f) above.
- (l) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (m) See (l) above.
- (n) See (l) above.

The following concentrations of sodium carbonate have not been harmful within the time specified:

<u>Concentration in mg/litre</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
33	5 days	Cutthroat trout	o
44	5 days	Silver salmon	p
58	5 days	King salmon	σ
100	7 days	Bass	r
200	7 days	Sunfish	s
200 to 500	7 days	Goldfish	t
500	7 days	Some goldfish	u

- (o) See (a) above.
- (p) See (a) above.
- (q) See (a) above.
- (r) See (d) above.
- (s) See (d) above.

(t) See (d) above.

(u) See (d) above.

Environmental Effects of Sodium Carbonate:

Sodium carbonate is highly soluble in water and dissociates into sodium and carbonate ions with a resulting increase in alkalinity and a tendency to raise the pH value. The carbonate ions will react with hydrogen ions until an equilibrium is established.

If sodium carbonate gains access to a watercourse, the following problems in the watercourse can be anticipated:

- (i) an increase in pH
- (ii) an increase in sodium concentration
- (iii) an increase in carbonate concentration
- (iv) an increase in total dissolved solids concentration

(7) Name: Sodium Hydroxide (Also known as Caustic Soda)

Formula: NaOH

Physical and Chemical Characteristics:

Solid NaOH

Molecular Weight	40.0
Equivalent Weight	40.0
Specific Gravity	2.13

Melting Point	318°C (605°F)
Boiling Point	1390°C (2534°F)
Latent Heat of Fusion	72 B.T.U. per pound 40 cal. per gram
Refractive Index	1.3576
Solubility in grams per 100 ml.	
	Cold water at 0°C 42
	Hot water at 100°C 347

Anhydrous sodium hydroxide is extremely hygroscopic and when exposed to the atmosphere absorbs moisture rapidly. In the presence of moisture, it reacts readily with carbon dioxide in the air to form hydrated sodium carbonate.

When crystallized from solution, the anhydrous material and all the hydrates are colourless; the commercial flake and solid forms, when solidified from the molten state, have a crystalline fracture and appear white and translucent.

NaOH in Solution

Sodium hydroxide is readily soluble in water with the evolution of a considerable amount of heat.

Solutions of sodium hydroxide in water are available to industry. Nominal 50 percent caustic soda is a solution containing approximately 50 pounds of NaOH in 100 pounds of solution. The specific gravity of a 50 percent (by weight)

NaOH solution is 1.530 at 60°F.

Sodium hydroxide is a strong alkali and, as a result, it will react violently with acid.

Iron, nickel and their alloys are only slightly corroded by sodium hydroxide solutions but other metals such as aluminum, tin and zinc react to form the sodium compounds of the metal such as sodium aluminate, sodium stannate and sodium zincate.

Hazards of Handling Sodium Hydroxide:

Sodium hydroxide in any form can produce a severe burn when it comes in contact with any part of the body. Contact with eyes causes serious injury.

Uses of Sodium Hydroxide in the Mining Industry:

Large volume uses of sodium hydroxide in mine-mill circuits are rare. It is, however, used almost exclusively as an alkalinity-control agent in the flotation of gold ores and non-metallic minerals with which lime or sodium carbonate do not perform satisfactorily.

Toxicity of Sodium Hydroxide:

The following concentrations of sodium hydroxide have been reported to have killed fish:

<u>Concentration in mg/litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
20	--	--	Silver salmon	a
25	--	24 hours	Brook trout	b
35	--	--	Cutthroat trout	c
40	Fresh	24 hours	Creek chub	d
48	--	--	King salmon	e
70	Stagnant	5 hours	Fish, Crabs	f
71.5	--	--	Carp, Shiners, Suckers	g
90	Circulating	4.5 hours	Fish, Oysters	h
96	Tap	2 to 10 hours	Carp, Shiners, Suckers	i
99	Tap	48-hour TL _m	Bluegill sunfish	j
100	--	--	Minnows	k
100	--	--	Fish	l
100	--	120 hours	Shiners	m
100	--	3 to 20 hours	Goldfish, Bass	n
125	Turbid	96-hour TL _m	Mosquito-fish	o
180 (ph 12)	Circulating	23 hours	Fish, Oysters	p

- (a) Hayder, E.P., Amberg, H.R., and Dimick, R.E., "The Effect of Kraft Mill Waste Components on Certain Salmonoid Fishes of the Pacific Northwest", Tech. Assn. Pulp and Paper Ind. (1962).

Dimick, R.E., "The Effects of Kraft Mill Waste Liquors and Some of Their Components on Certain Salmonoid Fishes of the Pacific Northwest.

- (b) Belding, D.L., "Toxicity Experiments With Fish in Reference to Trade Waste Pollution", Trans. Amer. Fish. Soc. (1927).
- (c) See (a) above (both references).
- (d) Gillette, L.A., Miller, D.L., and Redman, H.E., "Appraisal of a Chemical Waste Problem by Fish Toxicity Test", Sewage and Industrial Wastes (1952).
- (e) See (a) above (both references).
- (f) Daugherty, F.M., Jr., "Effects of Some Chemicals Used in Oil Well Drilling on Marine Animals", Sewage Works Jour. (1951).
- (g) See (b) above.
- (h) See (f) above.
- (i) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (j) Turnbull, H., DeMann, J.G., and Weston, R.F., "Toxicity of Various Refinery Materials to Fresh Water Fish", Symposium on Waste Disposal in the Petroleum Industry, Ind. Eng. Chem. (1954).
- (k) Anon., "The Toxicity of Kraft Pulping Wastes to Important Fish Food Species of Insect Larvae", National Council for Stream Improvement Tech. Bull. (July 1949).

Van Horn, W.M., Anderson, J.B., and Katz, M., "The Effect of Kraft Pulp Mill Wastes on Some Aquatic Organisms", Trans. American Fisheries Soc. (1949).

Van Horn, W.M., "The Effect of Pulp and Paper Mill Wastes on Aquatic Life", Fifth Ontario Industrial Wastes Conf., OWRC (1958).

- (l) Anon., "A Study of the Toxic Components of the Waste Waters of Five Typical Kraft Mills", National Council for Stream Improvement Tech. Bull. (May 1948).

Gehm, H.W., "The Toxic Effects of Sulphate Pulp Waste Liquors on Fish and Other Aquatic Life", National Council for Stream Improvement, Tech. Bull (1945).

- (m) See (k) above (second reference).

- (n) Keller, E.L., Simmonds, F.A., and Baird, P.K., "Some Observations on the Effect of Alum on Certain Sheet Properties of Paper", Paper Trade Jour. (1941); Water Poll. Abs. (February 1941).

- (o) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to Gambusia affinis of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).

- (p) See (f) above.

The following concentrations of sodium hydroxide have not harmed fish within the time specified:

<u>Concentration in mg/litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
10	--	--	Cutthroat trout	a
11	--	--	Silver salmon	r
20	Fresh	24 hours	Creek chub	s
27	--	--	King salmon	t
50	Distilled	2 hours	Perch, Roach	u
50	--	7 days	Goldfish, Bass	v
55.5	--	--	Carp, Shiners, Suckers	w
200	--	5 hours	Some fish	x

- (q) See (a) above (both references).
- (r) See (a) above (both references).
- (s) See (d) above.
- (t) See (a) above (both references).
- (u) See (i) above.
- (v) See (n) above.
- (w) See (b) above.
- (x) See (f) above.

Researchers have indicated that sodium hydroxide is not lethal to fully developed fish in natural fresh waters unless the pH value is well over 9.

Environmental Effects of Sodium Hydroxide:

If sodium hydroxide gains access to a watercourse, the following problems in the watercourse can be anticipated:

- (i) an increase in pH
- (ii) an increase in sodium concentration
- (iii) an increase in total dissolved solids concentration

SULPHIDE FLOTATION CHEMICALS

Froth flotation is a physico-chemical method of concentrating finely ground ores. The process involves the chemical treatment of an ore pulp to create conditions favourable for the attachment of specific mineral particles to air bubbles. The air bubbles carry the selected minerals to the surface of the pulp and form a mineralized froth which is skimmed off (to form a concentrate). Other unwanted minerals remain submerged in the pulp and are discharged as waste.

The basic elements of the type of machine that is used to accomplish sulphide ore flotation in the mining industry are shown in Figure 1. The ore particles, usually ground to minus 48 mesh (less than 295 microns or 0.295 mm. in diameter), are introduced into a flotation 'cell' (i.e., one flotation machine) in the form of a water slurry or 'pulp' at about 25 to 40 percent solids by weight. Generally, many individual flotation cells in series are used to allow sufficient time for all the valuable mineral or minerals to float. Air is introduced through the central shaft of a flotation machine and is dispersed into the well-mixed pulp

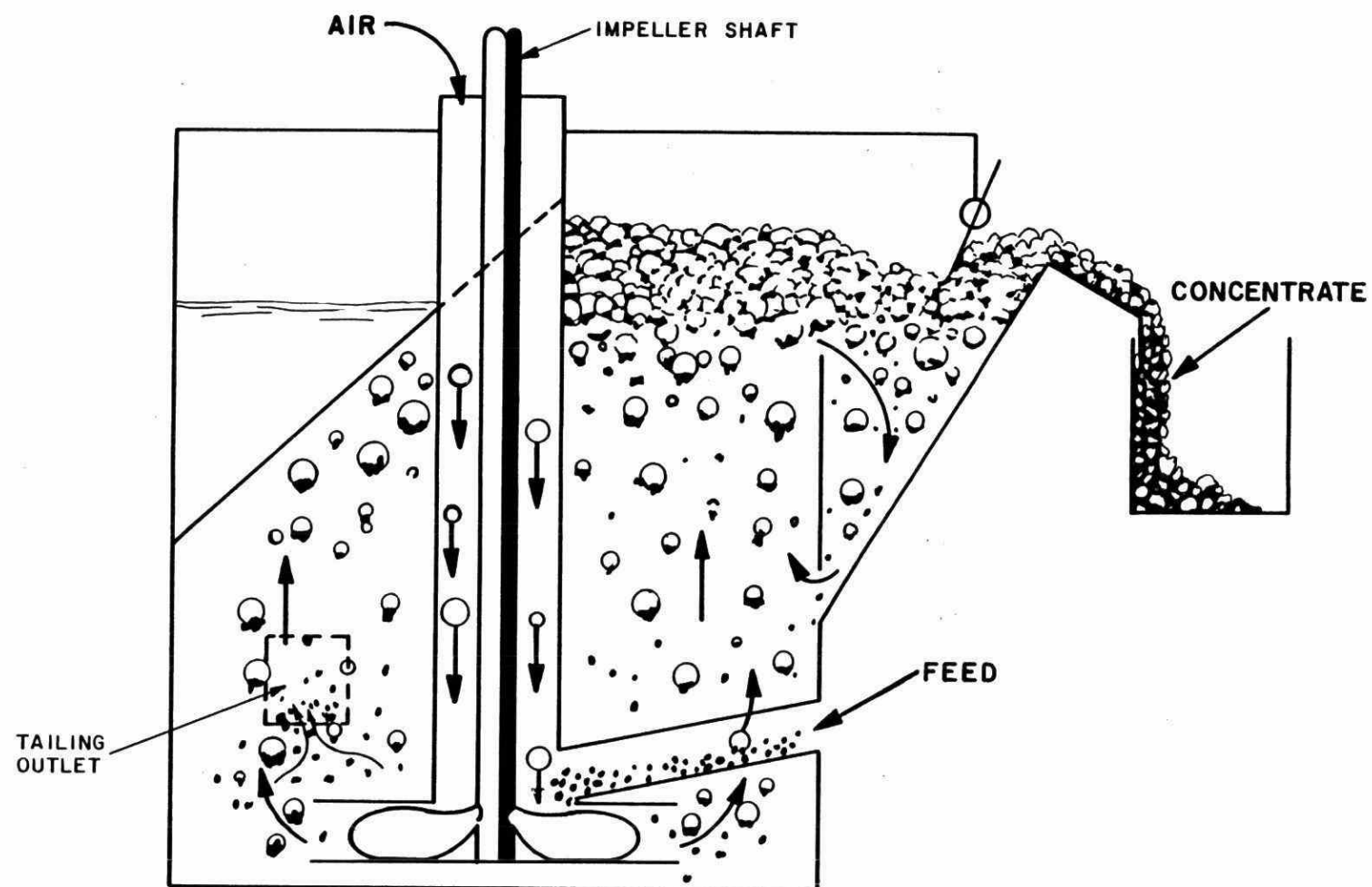


FIG. N°1
SIMPLIFIED FROTH FLOTATION CELL

by an impeller. The various chemicals that are required to enhance the flotation process are either added to the pulp before a flotation cell or are added by stages to a bank of flotation cells.

All flotation processes are selective or differential in that one mineral or group of minerals is floated away from associated unwanted material. Ordinarily, however, the separation of unlike minerals, such as sulphides from non-sulphides, is referred to as bulk flotation and the term differential flotation is restricted to operations involving separations of similar mineral types (for example, the production of individual copper sulphide, lead sulphide and zinc sulphide concentrates from a single copper-lead-zinc sulphide ore).

Froth flotation circuits vary greatly in use, size and complexity. The general nature of flotation circuits can, however, be illustrated by the following very simple example (see Figure 2):

After grinding, the feed (an uncomplicated lead-zinc ore) enters the first group of flotation cells at No. 4. Cells 4 to 10 are referred to as 'roughers'. The froth

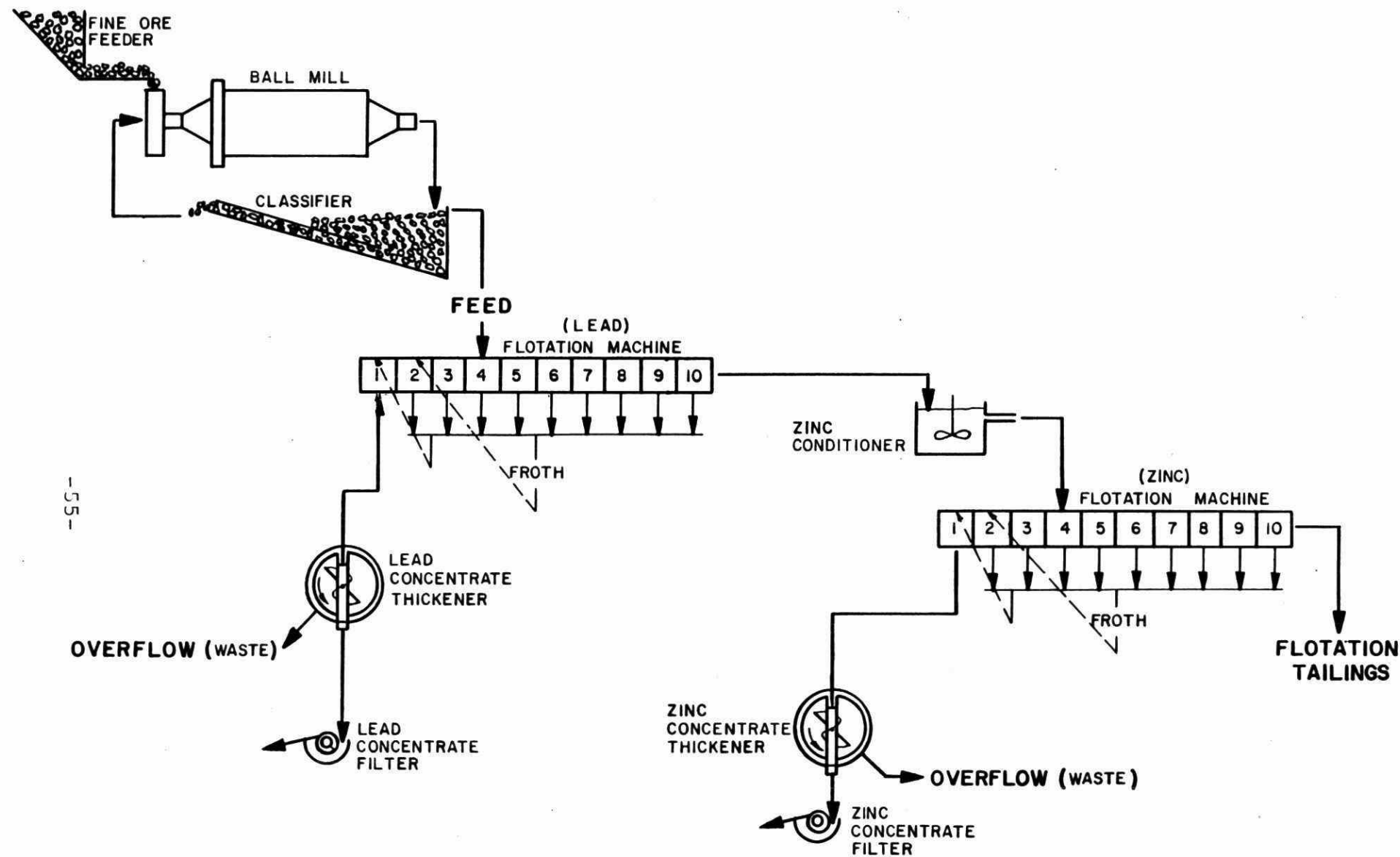


FIG. N° 2
SIMPLIFIED FLOWSHEET FOR TREATING
A LEAD - ZINC ORE

concentrate from these cells is sent to cells 2 and 3, called 'cleaners', to be refloated and then is refloated again in a 're-cleaner' cell (No. 1) to produce a lead (sulphide) concentrate. The nonfloated material or underflow passes from left to right to produce a final lead tailing from cell No. 10. Tailings from the lead flotation circuit are then 'conditioned' (mixed intimately) with specific chemicals prior to zinc flotation. The lead tailings are floated in 'roughers' and 'cleaners' as before. The result is a zinc (sulphide) concentrate and final mill tailings.

Figure 3, a diagram of the main circuits for flotation of nickel-copper sulphide ores in the Sudbury district of Ontario, indicates the basic variety to be expected in the flotation of ores. Figure 4 serves to indicate the actual complexity of an operating sulphide mill.

Most orebodies consist of from one to five economically extractable metals or minerals in a matrix of gangue (non-valuable) material. The physical association of the minerals in an ore is one of the most important factors with regard to flotation practice for it determines whether

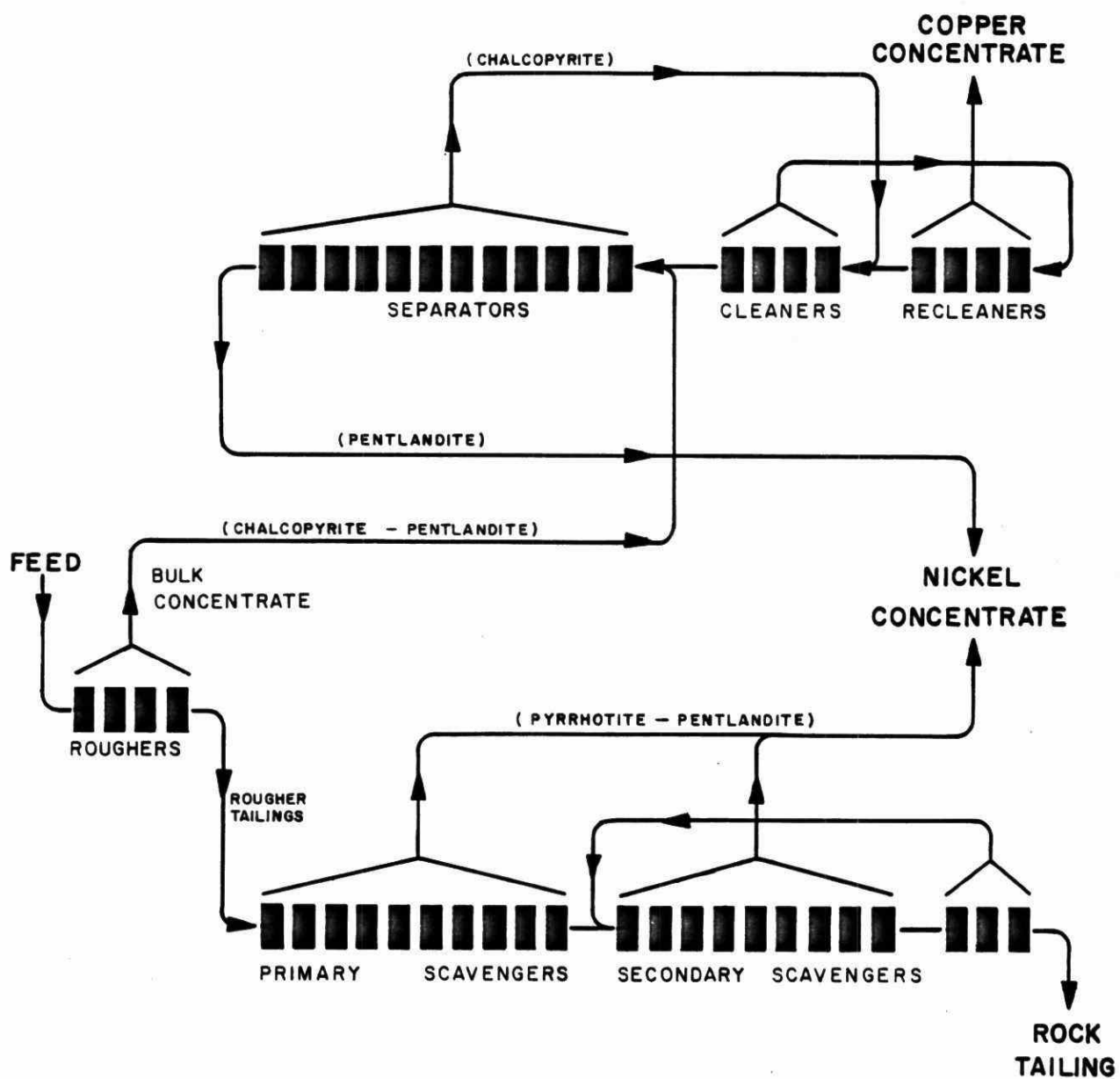


FIG. N° 3
 DIAGRAM OF MAIN CIRCUITS FOR
 FLOTATION OF NICKEL-COPPER
 SULFIDES

or not the valuable constituents of an ore may be economically recovered by flotation and it determines the complexity of the separation.

Flotation circuits are somewhat sensitive to fluctuations in the composition of mill feed and to abnormal changes in circuit chemistry. While no two orebodies are identical in composition, it is also true that no single orebody is consistent in composition throughout its mass. As a result, it is frequently necessary to simultaneously mine from various sections of an orebody and to blend the resultant broken ore into a relatively uniform feed for the mill.

The extensive substitution of foreign elements in a mineral crystal lattice, the adsorption of interfering ions, fine intergrowths of different mineral species, and the presence of mineral slimes which coat surfaces of minerals often make flotation separations very difficult.

Many commonly known chemical compounds are used for various purposes in froth flotation circuits in the Province of Ontario. Of more interest, however, is the great number of less commonly known relatively unusual

chemical compounds that find use in froth flotation circuits.

Most flotation chemicals fall into at least one of the three following categories:

- (1) Frothers
- (2) Collectors (Promoters)
- (3) Modifiers

A detailed discussion of each of these categories now follows:

FROTHERS

In a flotation cell, the production of a persistent froth of desired selectivity is extremely important. Involving the introduction of small air bubbles into the flotation pulp and collection of the unbroken mineral-laden bubbles on the surface of the pulp in the cell, the requisite frothing action is enhanced by the addition of a specific type of chemical, called a frother, into the ore pulp. In effect, a frother is a chemical that acts to produce a froth of satisfactory stability. The frother toughens the bubble wall (which is stabilized further by the mineral particles adhering to it) and thus prolongs the life of each bubble. A useful frother creates a froth which survives long enough

to permit the removal of its mineral load and yet breaks down within a reasonable length of time so that a permanent foam is not created.

Although some inorganic substances may cause frothing, the really effective agents are organic substances. In general, frothing agents have structural formulae that are characterized by the presence of two constituents having opposite properties: one part of the molecule is nonpolar, and the other is polar. Typical examples are amyl alcohol, $C_5H_{11}.OH$, cresol, $CH_3.C_6H_4.OH$, and toluidine, $CH_3.C_6H_4.NH_2$.

The frothing properties are related to the composition and structure of both parts of the molecule. Among homologous substances (i.e., substances having the same general structure, and therefore the same polar group, but varying hydrocarbon chains), the frothing ability at the concentration which yields maximum frothing increases with increase in the length of the hydrocarbon chain, up to a certain point, but decreases if the length of the chain becomes very great. This is particularly well shown in the series of the aliphatic alcohols, in which frothing increases with increase in the length of the hydrocarbon chain, up to

the 7 or 8-carbon-atom alcohol, but decreases thereafter. Substances having the same polar group and about the same solubility, but different structure in the nonpolar part of the molecule, have somewhat similar frothing qualities. Thus, hexyl alcohol, $C_6H_{13}OH$, or heptyl alcohol, $C_7H_{15}OH$, is roughly equivalent to terpineol, a cyclic terpene alcohol, $C_{10}H_{17}OH$.

Frothing can be traced directly to the dual character of frother molecules which have one water-avid and one water-repellent portion. Both these affinities are satisfied if the molecules occur at bubble walls with their polar, hydrated end adhering to the water phase and their nonpolar end away from it, so that frother molecules concentrate at the interface between the fluid phases of flotation systems. As a result of the addition of a frother, the gas bubbles formed under the surface of a liquid are partly lined with a monomolecular sheath of frother molecules. This allows each bubble with its lining to approach other bubbles without coalescing. To some extent, the effect produced by the addition of a frother is proportional to the amount of frother. However, past a certain point, the effect of

further additions of frother is less than that of preceding additions. Eventually, the addition of further amounts results in a decrease of the frothing action, and finally in the total absence of frothing. The point at which total absence of frothing is obtained corresponds to the saturation by the dissolved substances of the solutions.

The constituents of frothers are volatile substances, and many are pleasantly fragrant. They are in fact found also in the so-called essential oils which are used extensively in perfumery. Accordingly, a substantial part of the frothers added in flotation operations is volatilized so that re-use of flotation tailing waters does not necessarily reduce proportionately the requirement for frothers.

Generally speaking, it is desirable that a frother does not display a significant 'collecting' ability (see section concerning Collectors). However, under some circumstances, a frother with a collecting ability may be used to advantage.

Water-insoluble, saturated hydrocarbons such as kerosene will not form a suitable froth. Unsaturated hydrocarbons tend to form a light froth. Organic compounds such

as pine oil, alcohols, phenols, and fatty acids generally form appreciable amounts of relatively stable froth.

In practice, the most widely used frothers are pine oil, cresylic acid and certain synthetic alcohols.

Locally, eucalyptus oil (Australia) and camphor oil (Japan), etc., may be used as frothers. A class of reagents known as froth stiffeners can impart stability to a froth in some circumstances. Creosotes are typical of these materials.

SPECIFIC FROTHING AGENTS FINDING USE IN THE PROVINCE OF ONTARIO

(1) Pine Oil

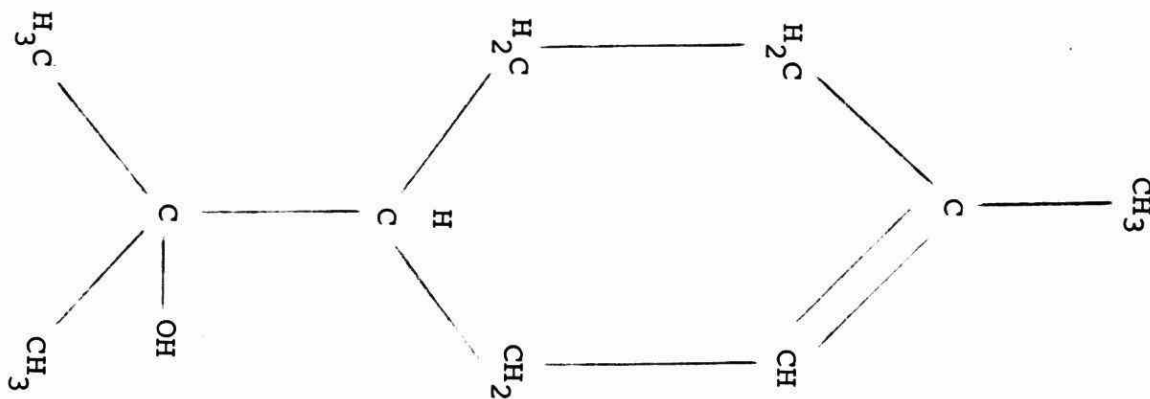
Pine oils are of several varieties and include those obtained from the destructive distillation and steam distillation of pine. Recent practice has tended to favour the use of steam-distilled pine oil instead of destructively-distilled oil.

Steam-distilled pine oil is composed essentially of terpene hydrocarbons, terpene ketones, and terpene alcohols; in particular terpene, pinene, citronellol, and terpineol. The terpene alcohols of pine oils are more soluble than the terpene hydrocarbons, produce a froth having a regular cell structure, and have low collecting

properties. Alphaterpineol is available industrially at a reasonable cost and is superior to pine oil as a pure frother.

Pine oil is still widely used as a frother in sulphide flotation. It exhibits some collecting properties, especially for readily floatable minerals such as talc, sulphur, graphite and molybdenite. The froth produced by pine oil is tougher and more persistent than that produced by cresylic acid. The main undesirable characteristic of pine oil is its tendency to float gangue.

Alphaterpineol is the dominant terpene alcohol in pine oil. In its structure, shown below, the hydroxyl (OH) is the polar group.



Specific Pine Oil Commercial Products

Product Name: Yarmor F

Yarmor 350

Company: Hercules

Typical Properties:

	<u>Yarmor F</u>	<u>Yarmor 350</u>
Colour	pale yellow	pale yellow
Specific Gravity at 15.6/15.6°C	0.937	0.905
Refractive Index at 20°C	1.484	1.479
Moisture %	less than 1	less than 1
Viscosity, cps., at 25°C	14.2	2.8
Density, lb./gal., at 25°C	7.8	7.5
Freezing Point, °C	-10	-15
Flash Point, Cleveland open cup, °C (°F)	76 (169)	63 (145)
Distillation Range, °C		
5%	200	186
50%	211	202
95%	222	220

Toxicity of Pine Oil

Little information has been generated concerning the toxicity of pine oil and pine oil products. The following, however, concerning the toxicity and biodegradability of

pine oil was supplied by one company (Hercules) and does give a very valuable indication of the toxicity of pine oil and pine oil-based products. The information is quoted verbatim from a company publication:

"The statements below, from the laboratories of Ryckman, Burbank, Edgerley and Associates (St. Louis, Missouri) summarize their biodegradability studies on Hercules Yarmor, a typical high grade commercial pine oil. The studies were conducted to establish a basis for reply to the question "Is this product biodegradable?" Typical products or wastes were chosen and a test program was designed to determine the effects these materials might have if the product was discharged into a watercourse or sewage treatment plant. The fish toxicity of the product was tested before and after treatment with a laboratory scale sewage treatment plant.

The Yarmor pine oil was introduced in the following systems in the form of a mixture comprised of 80% pine oil, 10% fatty acid soap, and 10% water.

Fish Toxicity: 46-69 ppm was a median lethal concentration to bluegill fingerlings when exposed for 24-48 hours.

This same species of fish survived when exposed to an effluent of an activated sludge treatment plant which was fed 50 ppm of contaminant (pine oil). This fact confirms the removal suggested by a river die away study.

River Die Away: If pine oil was discharged into a surface body at a concentration of 5 ppm, the contaminant would be degraded to approximately the same extent as sewage with about half of it decaying each 6.5 days. Fish toxicity would not be expected. (5-day B.O.D. = 0.8 mg. oxygen/mg. pine oil).

Reactions Within Sewage Treatment Plant: When introduced into a simulated activated sludge sewage treatment plant at a concentration of 50 ppm, the pine oil was decomposed at a rate of 50% per 24 hours.

To summarize these data on pine oil, the material can be called degradable and if it were discharged into a surface water, the fish life should not be affected. Normal household sewage which contains pine oil would be slowly degraded in an activated sludge sewage plant without detrimental effects on the treatment plant or the microorganisms present in sludge. The effluent from such a plant would not

be harmful to fish because of the presence of pine oil."

(2) Cresylic Acid

The cresylic acids of commerce are composed of a number of higher homologs of phenol, $C_6H_5.OH$, particularly cresols, $CH_3.C_6H_4.OH$, and xylenols, $C_2H_5.C_6H_4.OH$, or $(CH_3)_2.C_6H_3.OH$. In most cresylic acids of commerce, the xylenols are the dominant constituents.

Cresylic acid is still a popular frother. Its frothing power varies and is generally related to its distillation range (the lower ranges produce a lighter less persistent froth than do the higher ranges).

Cresylic acid is a powerful frother and, unlike the alcohol frothers, it has some collecting properties and, therefore, tends to be nonselective. It is used where persistent froth is required and selectivity is not a problem.

The physical characteristics of cresylic acid are as follows:

Colour - yellow-dark

Specific Gravity - 1.01 to 1.04

Boiling Point $^{\circ}C$ - 190 to 235

Flash Point $^{\circ}C$ (Cleveland Open Cup) - 150

Toxicity of Cresylic Acid

Cresylic acid at a concentration of 0.1 mg/litre killed goldfish in hard water in five days and at a concentration of 1.0 mg/litre in 6 to 48 hours. In soft water, 0.1 mg/litre killed Daphnia in 72 hours. (a)

Chinook, silver, and pink salmon were exposed for three days in both sea water and fresh water to varying concentrations of refined and crude cresylic acid. (b) Concentrations of 3.12 to 6.98 mg/litre gave 100 percent kills, and the critical levels were estimated to be as low as 1.65 mg/litre. Using a commercial impure o-cresylic acid, Clemens and Sneed (c) found the 96-hour TL_m toward fingerling channel catfish to be 11.2 mg/litre at 21°C. No fish were killed by 4.0 mg/litre and all succumbed to 15.8 mg/litre. Using refined cresylic acid, the Washington State Department of Fisheries (d) found that concentrations of 3.12 to 6.60 mg/litre killed most of the chinook and silver salmon exposed for three days in both fresh water and sea water. Critical levels were given as 1.65 to 3.40 mg/litre. With crude cresylic acid, the lowest concentrations causing a significant kill varied from 3.27 to 8.69 mg/litre and the critical

levels were estimated at 3.27 to 6.1 mg/litre.

- (a) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (b) Anon., "Toxic Effects of Organic and Inorganic Pollutants on Young Salmon and Trout", State of Washington Dept. Fisheries Res. Bull. (1960).
- (c) Clemens, H.P., and Sneed, K.E., "Lethal Doses of Several Commercial Chemicals for Fingerling Channel Catfish", Special Scientific Report Fisheries, U.S. Dept. of Interior (1959).
- (d) See (b) above.

Since cresols are active frothers in cresylic acid, toxicity information concerning cresols is presented below. Cresols are colourless oily liquids or crystalline solids. There are three isomers (ortho, meta, para) of cresol and all are highly soluble in water.

The reported effects of ortho, meta and para-cresol on fish are shown in the following tabulations:

<u>Concentration in mg/litre</u>	<u>Type of Fish</u>	<u>Effect</u>	<u>Reference</u>
Ortho cresol			
2.3	Salmonide embryos	24-hour TL _m , approx.	a
4.0-5.0	Minnows	Detected and avoided	b
10	Perch	Lower toxic limit, 15°C	c
11.2	Fingerling catfish	96-hour TL _m , 21°C	d
15.4-15.8	Tench, bleak	24-hour TL _m , approx.	e
17	Perch	Immobilized in 10 min., 15°C	f
20	Minnows	Immobilized in 54 min., 15°C	g
24	Fathead Minnows	48-hour TL _m	h
29.5	Carp	24-hour TL _m , approx.	i
55-65	Sunfish	Killed in one hour	j
60	Minnows	Killed, 17°C	k
66.8	Fingerling catfish	72-hour TL _m , 21°C	l
70	Roach	Killed in 3 hours, 21°C	m
110	Roach	Killed in 5 hours, 9.5°C	n
Meta cresol			
6.5	Salmonide embryos	24-hour TL, approx.	o
10	Perch	Lower toxic _m limit, 15°C	p
19	Perch	Immobilized in 10 min., 15°C	q
20	Minnows	Immobilized in 38 min., 15°C	r
21	Tench, bleak	24-hour TL _m , approx.	s
24.5	Carp	24-hour TL _m , approx.	t
Para cresol			
4.0	Salmonide embryos	24-hour TL, approx.	u
4.0-5.0	Minnows	Detected and avoided	v
5.0	Rainbow trout	Killed, 17°C	w
7.5	Yearling trout	Toxic limit, 1 hour 13°C	x
10	Perch	Lower toxic limit, 15°C	y
10-15	Perch	Killed	z
15.4-15.8	Tench, bleak	24-hour TL _m , approx.	aa
20	Perch	Immobilized in 10 min., 15°C	ab
20	Minnows	Immobilized in 21 min., 15°C	ac
20	Minnows	Killed, 17°C	ad
21.2	Carp	24-hour TL _m , approx.	ae
80-90	Sunfish	Killed in one hour	af
100	Minnows	Killed in 30 min.	ag

<u>Concentration in mg/litre</u>	<u>Type of Fish</u>	<u>Effect</u>	<u>Reference</u>
b) Isomer not given			
8-10	Minnows	Min. lethal dose, 6 hours, dist. water 20°C	ah
10.0-13.6	Bluegill sunfish	96-hour TL _m , 20°C	ai
10-15	Fish	Killed	aj
10-20	Goldfish	Killed in 3-5 days, hard wtrs.	ak
21-14	Minnows	Min. lethal dose, 6 hours, hard water, 20°C	al
17-20	Fish	Killed	am
22	Mosquito-fish	96-hour TL _m , turbid water, 17-20°C	an
26	Brook trout	Killed in 5.5 min., 22.5°C	ao

One observer, noting that 10 mg/litre killed fish, also reported that 0.5 mg/litre had no appreciable effect.

The toxicity of cresols to fish appears to vary with the dissolved-oxygen content of the water, with low oxygen being synergistic (ap). Thus, 6.2 mg/litre of para-cresol in tap water caused trout to float helplessly in 100 minutes when the dissolved oxygen was 10 mg/litre; but when the dissolved oxygen was only 3.0 mg/litre, the trout succumbed in 13 minutes (aσ).

Southgate (ar) studied the toxicity of mixtures of KCN and p-cresol to trout. These substances do not appear

to be synergistic, but exert an independent action on fish. Furthermore, concentrations of p-cresol and phenol of equivalent toxicity are interchangeable and appear to exert their toxic action on trout in the same manner. Para-cresol and 1, 2, 6-xyleneol are only partly interchangeable. Sub-lethal concentrations of 1, 2, 6-xyleneol increase the toxicity of p-cresol but sub-lethal concentrations of p-cresol do not appreciably affect the toxicity of xyleneol.

Clendenning and North (as, at, au) investigated the effects of cresols on the giant kelp, *Macrocystis pyrifera*. The concentration required to cause a 50-percent inactivation of photosynthesis in bottom kelp fronds during a four-day exposure was 5-10 mg/l. Para-cresol was slightly less toxic than o- or m-cresol.

- (a) Albersmeyer, W., and Erichsen, L.V., "Investigations on the Effects of Tar Constituents in Waste Waters", Z. Fisch. (1959).
- (b) Jones, J.R.E., "The Reactions of the Minnow (*Phoxinus phoxinus* L.) to Solutions of Phenol, Ortho-Cresol and Para-Cresol", Jour. Exp. Bio. (1951).
- (c) Bucksteeg, W., Thiele, H., and Stoltzel, K., "The Effect on Fish of Toxic Substances in Waste Waters", Vom Wasser (1955).

- (d) Clemens, H.P., and Sneed, K.E., "Lethal Doses of Several Commercial Chemicals for Fingerling Channel Catfish", Special Scientific Report, Fisheries, U.S. Dept. of Interior (1959).
- (e) See (a) above.
- (f) See (c) above.
- (g) See (c) above.
- (h) Black, H.H., McDermott, G.N., Henderson, C., Moore, W.A., and Pahren, H.R., "Industrial Waste Guide, By-product Coke", Proc. 11th Industrial Waste Conf., Purdue University (1957).
- (i) See (a) above.
- (j) Shelford, V.E., "An Experimental Study of the Effects of Gas Waste Upon Fishes, With Especial Reference to Stream Pollution", Bull. Ill. State Lab. Nat. Hist. (1917).
- (k) Jones, J.R.E., "Fish and River Pollution", Chapter 7 of "Aspects of River Pollution", L. Klein, Editor, Butterworth Scientific Publ. (1957).
- (l) See (d) above.
- (m) Hubault, E., "The Toxicity of Various Phenols Towards Fresh Water Fish", C.R. Acad. Agr. Fr. (1936); Water Pollution Abs. (1936).
- (n) See (m) above.
- (o) See (a) above.
- (p) See (c) above.
- (q) See (c) above.
- (r) See (c) above.

- (s) See (a) above.
- (t) See (a) above.
- (u) See (a) above.
- (v) See (b) above.
- (w) See (k) above.
- (x) Anon., "The Preparation of Non-toxic Tar", Jour. Society Chem. Ind. (1937).
- (y) See (c) above.
- (z) Anon., "Joint Committee on Damage to Fisheries, Road Tars and Fish Life", Surveyor (1930).
- (aa) See (a) above.
- (ab) See (c) above.
- (ac) See (c) above.
- (ad) See (k) above.
- (ae) Hoak, R.D., "The Causes of Tastes and Odors in Drinking Water", Water and Sewage Works (1957).
- (af) See (j) above.
- (ag) See (b) above.
- (ah) Le Clerk, E., "The Self-Purification of Streams and the Relationship Between Chemical and Biological Tests", Proc. of the 2nd Symposium on the Treatment of Waste Waters, Pergamon Press (1960).
- (ai) Anon., "The Relationship of Body Size of the Bluegill Sunfish to the Acute Toxicity of Some Common Chemicals", Philadelphia Academy of Sciences (1956).

- (aj) Ebeling, G., "Stream Pollution (Rhine River, Germany)", Vom Wasser (1939); Chem. Abs. (1941).
- (ak) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (al) See (ah) above.
- (am) See (ak) above.
- (an) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to Gambusia Affinis of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (ao) Embody, D.R., Schuck, H.A., Crump, S.L., Freese, J.W., Ross, L., "Effect of Cresol on Brook Trout, *Salvelinus fontinalis*", Trans. American Fisheries Soc. (1940).
- (ap) Southgate, B.A., Pentelow, F.T.K., and Bassindale, R., "The Toxicity to Trout of Potassium Cyanide and p-Cresol in Water Containing Different Concentrations of Dissolved Oxygen", Biochem. Jour. (1933).
- (aq) See (ak) above.
- (ar) Southgate, B.A., "The Toxicity of Mixtures of Poisons", Quarterly Jour. Pharm. and Pharmacology (1932); Water Pollution Abs. (1933).
- (as) Clendenning, K.A., and North, W.J., "Effect of Wastes on the Giant Kelp, *Macrocystis pyrifera*", Proc. 1st Int. Conf. on Waste Disposal in the Marine Environment, Pergamon Press (1960).
- (at) Kibalchich, I.A. et al., "Sanitary Assessment of the Consequences Resulting from the Flooding of Tree Vegetation During Preparation of Water Reservoir Beds", Hygiene and Sanitation (Moscow) (1960); Jour. A.W.W.A. (1961).

- (au) North, W.N., Clendenning, K.A., and Scotten, H.L.,
 "The Effects of Waste Discharges Upon Kelp", Quarterly
 Progress Report (1 July 1959 - 30 Sept. 1959). Inst. of
 Marine Resources, Calif.

Toward lower aquatic life, the following effects of
 cresols have been reported:

<u>Concentration</u> <u>mg/litre</u>	<u>Isomer</u>	<u>Organism</u>	<u>Effect</u>	<u>Reference</u>
5	p	Scenedesmus	Toxic threshold, 24°C	a
10	-	Crustacea	Killed in two hours	b
10	p	Microregma	Toxic threshold	c
10	-	Gammaridae	Not affected	d
12	p	Daphnia	Toxic threshold, 23°C	e
16	o	Daphnia	Toxic threshold, 23°C	f
20	m	Microregma	Toxic threshold	g
20-30	-	Culex larvae	Reaction threshold	h
25	-	Gammaridae	Killed	i
28	m	Daphnia	Toxic threshold, 23°C	j
30-40	-	Daphnia pulex	Reaction threshold	k
40	o	Scenedesmus	Toxic threshold, 24°C	l
40	m	Scenedesmus	Toxic threshold, 24°C	m
50	o	Microregma	Toxic threshold	n
30-100	-	Sayomia plum. larvae	Reaction threshold	o
90-100	-	Pyonocypris vidua	Reaction threshold	p
100-120	-	Culex pupae	Reaction threshold	q
500	o	E. coli	Toxic threshold, 27°C	r
500	m	E. coli	Toxic threshold, 27°C	s
940	o	Bacteria	Inhibited oxygen utilization	t
1000	p	E. coli	Not affected, 27°C	u

- (a) Bringmann, G., and Kuhn, R., "The Toxic Effects of Waste
 Water on Aquatic Bacteria, Algae, and Small Crustaceans",
 Gesundheits-Ing. (1959).

- (b) Ellis, M.M., "Pollution of the Coeur d'Alene River and Adjacent Waters by Mine Wastes", U.S. Bur. Fish., Spec. Sci. Rept. (1940).
- (c) Bringmann, G. and Kuhn, R., "Water Toxicology Studies with Protozoans as Test Organisms", Gesundheits-Ing. (1959).
- (d) See (b) above.
- (e) See (a) above.
- (f) See (a) above.
- (g) See (c) above.
- (h) Albersmeyer, W., and Erichsen, L.V., "Investigations on the Effects of Tar Constituents in Waste Waters", Z. Fisch. (1959).
- (i) See (b) above.
- (j) See (a) above.
- (k) See (h) above.
- (l) See (a) above.
- (m) See (a) above.
- (n) See (c) above.
- (o) See (h) above.
- (p) See (h) above.
- (q) See (h) above.
- (r) See (a) above.
- (s) See (a) above.

(t) Hermann, E.R., "Toxicity Index for Industrial Wastes", Industrial Eng. Chem. (1959).

(u) See (a) above.

(3) Other Frothing Agents

(i) Name: Aerofroth 53 Frother

Company: Cyanamid

Chemistry: Unknown

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	100 to 1000 ppm ^v /v	relatively non-toxic

(ii) Name: Aerofroth 61 Frother

Company: Cyanamid

Chemistry: Unknown

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	greater than 1000 ppm ^v /v	relatively non-toxic

(iii) Name: Aerofroth 65 Frother

Company: Cyanamid

Chemistry: A water soluble product of the poly-glycol type

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1000 to 10,000 ppm ^v /v	relatively non-toxic

(iv) Name: Aerofroth 70 Frother

Company: Cyanamid

Chemistry: A six-carbon, branch-chain alcohol
(M.I.B.C.)

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	100 to 1000 ppm ^v /v	relatively non-toxic

(v) Name: Aerofroth 71 Frother

Company: Cyanamid

Chemistry: A mixture of 6 to 9-carbon alcohols

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	100 to 1000 ppm ^v /v	relatively non-toxic

(vi) Name: Aerofroth 73 Frother

Company: Cyanamid

Chemistry: An alcohol frother

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	32 to 320 ppm ^v /v	moderate

(vii) Name: Aerofroth 77 Frother

Company: Cyanamid

Chemistry: Straight-chain higher alcohols

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	10 to 100 ppm ^v /v	moderate

(viii) Name: The Dowfroth Frothers

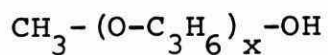
(Dowfroth 250)

(Dowfroth 200)

Company: Dow

Chemistry: Polypropylene glycol methyl ethers

The Dowfroth frothers may be
represented by the following formula:



The Dowfroth frothers are not single
chemical entities; rather, each con-
sists of a mixture of homologs of

varying molecular weight.

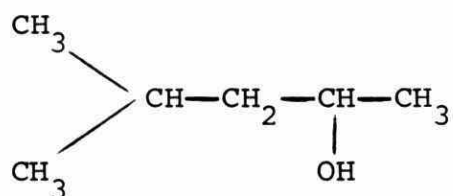
The first Dowfroth frothing agent produced was designated Dowfroth 250 with the number referring to the average molecular weight. Later, Dowfroth 200 (av. mol. wt. = 200) was introduced.

<u>Property</u>	<u>Dowfroth 200</u>	<u>Dowfroth 250</u>
Viscosity, 25°C, centipoises	6.2	-
(Initial) Boiling Point, °C	-	252
Freezing Point, °C	-78	-71
Flash Point, °F	250	285
pH	7.2	7.2

Toxicity (Dowfroth 250) (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	greater than 1,000 ppm ^v /v	relatively non-toxic

(ix) Name: M.I.B.C. (Methylisobutylcarbinol or Methyl Amyl Alcohol)



Company: Cyanamid (Aerofroth 70 Frother) (which see)

Chemcell

Union Carbide

Chemistry:

Molecular weight 102.17

Specific gravity, 20°/4°C 0.8065

Boiling point (760 mm Hg) 131.8°C

Freezing point -90°C

Solubility at 20°C

- M.I.B.C. in water 1.7% by weight

- water in M.I.B.C. 5.8% by weight

Flash point (closed cup) 41°C

M.I.B.C. is a stable colourless liquid. It is only slightly soluble in water but is miscible in all proportions with most organic solvents.

Toxicity of M.I.B.C.:

Tests performed on animals have shown that its toxicity is comparable to that of normal butyl alcohol.

NOTE: M.I.B.C. products typically contain 99.0% M.I.B.C. by weight and have a water content of approximately 0.1%

(x) Miscellaneous Frothing Agents

(i) Name: Dowfroth 1012

Company: Dow

Chemistry: Similar to Dowfroth 200 and 250. While Dowfroth 200 and 250 are completely soluble in water, Dowfroth 1012 is only partially soluble.

Physical Properties:

Avg. Mol. Wt.	400
Viscosity at 25°C, cps.	27
Sp. Gravity at 25/25°C	0.988
Initial Boiling Point at 760 mm Hg., °C	293
Freezing Point, °C	below -50
Flash Point, °F	375
pH	7.0

(ii) Name: Chemcell Frother CF-98

Company: Chemcell

Chemistry: Chemcell Frother CF-98 is a high boiling alcohol-type frother.

Physical Properties:

Initial Boiling Point	145°C
Specific Gravity 20/20°C	0.93
Water Content (% wt.)	0.49
Solubility in Water at 25°C, %	5.0

(iii) Name: UCAR Frother R-130

Company: Union Carbide

Chemistry: UCAR Frother R-130 is a high
molecular weight alcohol.

Typical Physical Properties:

Specific Gravity, 20/20°C	0.8205
Boiling Point, °C	157
Freezing Point, °C	-44.6
Solubility in Water at 20°C	0.6% by weight
Flash Point (Tag Open Cup) °F	149
Molecular Weight	102
Absolute Viscosity at 20°C	5.4 Centipoises
Average Weight per U.S. gallon	6.8 pounds

Toxicity:

Frother R-130 is not highly toxic by mouth. Tests on rats show that its toxicity range by mouth is the same as

ethyl ether. It is mildly irritating to the skin and is capable of causing eye burns.

(iv) Name: Poly propyleneglycol 425 Frother
Grade

Company: Union Carbide

(v) Name: UCAR Frother R-6

Company: Union Carbide

Chemistry: A straight chain C-6 alcohol

(vi) Name: Flotanol F

Company: Hoechst

Chemistry: Based on higher alcohols

(vii) Name: Flotanol G

Company: Hoechst

Chemistry: Developed from Flotanol F
and, although of the same
basis, it differs from
Flotanol F in being readily
miscible both with water and
with hydrocarbon oils; there-
fore it can, for example, be

used in dilute aqueous solution or extended with a light fuel oil.

(viii) Name: Flotol B
Company: Hoechst
Chemistry: A synthetic pine oil containing-
ing a guaranteed minimum 95%
content of terpene alcohols.

(ix) Name: Flotigol CS
Company: Hoechst
Chemistry: Based on phenol derivatives.

COLLECTORS (PROMOTERS)

Of flotation agents, the most important are the 'collectors' (sometimes called 'promoters') which attach themselves to specific normally non-floating minerals thus endowing them with hydrocarbon-like surfaces and making them capable of adhering to the gas bubbles that are generated by a flotation cell.

Natural floatability is exhibited by solids that possess an outer surface that is nonionic in character. For

practical purposes, this means a hydrocarbon surface. Collector molecules should therefore consist, at least in part, of hydrocarbon or similar groups.

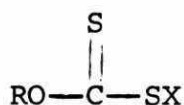
In practice, each collector molecule contains a polar and a non-polar group. When attached to a mineral particle, these molecules are so oriented that the non-polar or hydrocarbon group is extended outward. Such orientation results in the formation of a hydrophobic hydrocarbon film on the mineral surface.

Specific Collecting (Promoting) Agents

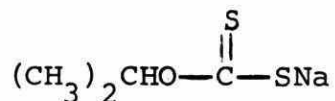
Group A: Xanthates

(a) General Information

Xanthates are dithiocarbonates corresponding to the structural formula



in which R represents the alkyl radical and X an alkali metal. For example, sodium isopropyl xanthate has the formula



The xanthates used in flotation are generally prepared from an aliphatic alcohol, carbon disulphide, and caustic soda or caustic potash.



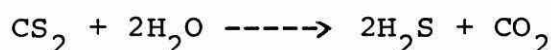
Oxidation of a xanthate results in the formation of the dixanthogen



The decomposition of xanthates in storage is generally due to the presence of water and is represented by the following general equation:



By further reaction, the Na_2CS_3 and CS_2 are converted to Na_2CO_3 and CO_2 with the release of H_2S as follows:

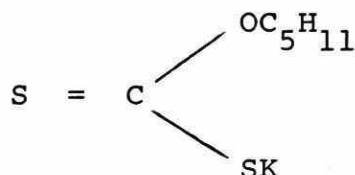


At temperatures above 30 degrees C, low concentrations (of xanthate), and exposure to acidic conditions, decomposition of xanthates is extremely rapid.

Xanthates are completely water soluble and are relatively stable solids. When pure, they are nearly white and have no odour. The commercial product, however, which ordinarily has undergone exposure to air, has a characteristic odour and may range in colour from near white to a deep yellow.

(b) Specific Information

(i) Potassium Amyl Xanthate



Toxicity (OWRC Lab. Value):

Product A

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	0.1 to 1.0 ppm ^{w/v}	high toxicity
N. Atherinoides	10 to 100 ppm ^{w/v}	moderate toxicity
P. Promelas	1.8 to 18 ppm ^{w/v}	moderate toxicity

Product B

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	18 to 180 ppm ^{w/v}	moderate toxicity

Commercial Products Based on Potassium Amyl Xanthate

Z - 6 (Dow)
Aero Xanthate 350 (Cyanamid)
CX - 51 (Chemcell)

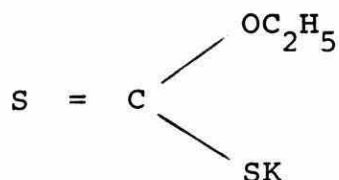
(ii) Potassium Sec-Amyl Xanthate

Toxicity: Not known

Commercial Products Based on Potassium Sec-Amyl Xanthate

Z - 5 (Dow)

(iii) Potassium Ethyl Xanthate



Toxicity (OWRC Lab. Value):

Product A

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	0.1 to 1.0 ppm ^w / _v	high toxicity
N. Atherinoides	0.01 to 0.1 ppm ^w / _v	high toxicity
P. Promelas	0.1 to 1.0 ppm ^w / _v	high toxicity

Product B

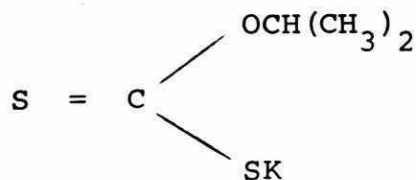
<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	0.56 to 5.6 ppm ^w / _v	high toxicity

Commercial Products Based on Potassium Ethyl Xanthate

Z - 3 (Dow)

Aero Xanthate 303 (Cyanamid)

(iv) Potassium Isopropyl Xanthate



Toxicity (OWRC Lab. Value):

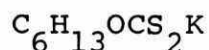
Product A

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	3.2 to 32 ppm ^w /v	moderate toxicity

Commercial Products Based on Potassium Isopropyl Xanthate

Z - 9 (Dow)

(v) Potassium Hexyl Xanthate



Toxicity (OWRC Lab. Value):

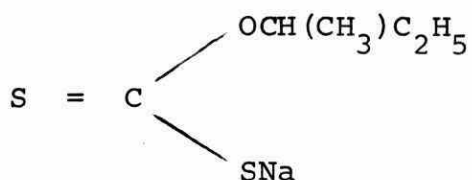
Product A

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	100 to 1000 ppm ^w /v	relatively non-toxic

Commercial Products Based on Potassium Hexyl Xanthate

Z - 10 (Dow)

(vi) Sodium Sec-Butyl Xanthate



Toxicity (OWRC Lab. Value):

Product A

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	32 to 320 ppm ^w /v	moderate toxicity

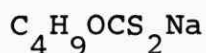
Product B

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	0.56 to 10 ppm ^w /v	high toxicity
N. Atherinoides	1.0 to 10 ppm ^w /v	moderate toxicity
P. Promelas	3.2 to 56 ppm ^w /v	moderate toxicity

Commercial Products Based on Sodium Sec-Butyl Xanthate

Aero Xanthate 301 (Cyanamid)
Z - 12 (Dow)
CX - 41 (Chemcell)

(vii) Sodium Isobutyl Xanthate



Toxicity (OWRC Lab. Value):

Product A

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	0.56 to 10 ppm ^w /v	high toxicity
N. Atherinoides	10 to 100 ppm ^w /v	moderate toxicity
P. Promelas	32 to 320 ppm ^w /v	moderate toxicity

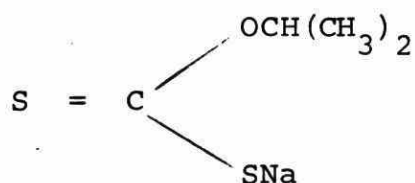
Product B

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	56 to 560 ppm ^w /v	moderate toxicity

Commercial Products Based on Sodium Isobutyl Xanthate

Aero Xanthate 317 (Cyanamid)
Z - 14 (Dow)

(viii) Sodium Isopropyl Xanthate



Toxicity (OWRC Lab. Value):

Product A

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	0.1 to 1.0 ppm ^w / _v	high toxicity
N. Atherinoides	0.01 to 0.1 ppm ^w / _v	high toxicity
P. Promelas	0.32 to 5.6 ppm ^w / _v	high toxicity

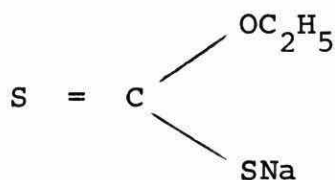
Product B

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	0.18 to 1.8 ppm ^w / _v	high toxicity

Commercial Products Based on Sodium Isopropyl Xanthate

CX - 31 (Chemcell)
Z - 11 (Dow)
Aero Xanthate 343 (Cyanamid)

(ix) Sodium Ethyl Xanthate



Toxicity (OWRC Lab. Value):

Product A

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	0.18 to 1.8 ppm ^w /v	high toxicity

Product B

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	0.1 to 1.0 ppm ^w /v	high toxicity
N. Atherinoides	0.01 to 0.1 ppm ^w /v	high toxicity
P. Promelas	0.32 to 3.2 ppm ^w /v	high toxicity

Commercial Products Based on Sodium Ethyl Xanthate

Z - 4 (Dow)
Aero Xanthate 325 (Cyanamid)
CX - 21 (Chemcell)

(c) Other Major Suppliers of Xanthates

(i) UBC (Belgium)

potassium ethyl xanthate
sodium ethyl xanthate
potassium isopropyl xanthate
sodium isopropyl xanthate
potassium normal butyl xanthate
sodium secondary butyl xanthate
potassium amyl xanthate

(ii) Hoechst (Germany)

potassium ethyl xanthate
sodium ethyl xanthate
potassium isopropyl xanthate
sodium isopropyl xanthate
potassium butyl xanthate
potassium isobutyl xanthate
sodium sec. butyl xanthate
potassium amyl xanthate
potassium hexyl xanthate
potassium octyl xanthate

Group B: Collectors Other Than Xanthates

- (i) Name: Aerofloat 15 Promoter
Aerofloat 25 Promoter
Aerofloat 31 Promoter
Aerofloat 33 Promoter
Aerofloat 242 Promoter

Company: Cyanamid

Chemistry: The above products are essentially aryl dithiophosphoric acids. Small amounts of a secondary promoter of limited solubility are included in Aerofloat 31, 33 and 242 Promoters.

Toxicity: Because of their limited solubility in water, the OWRC Lab. did not run bioassays on Aerofloat 15, 25, 31 and 33 Promoters.

The toxicity of Aerofloat 242 Promoter as determined at the OWRC Lab. is as follows:

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	10 to 100 ppm ^w / _v	moderate toxicity
P. Promelas	10 to 100 ppm ^w / _v	moderate toxicity

- (ii) Name: Sodium Aerofloat Promoter

Company: Cyanamid

Chemistry: Sodium diethyl-dithiophosphate

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	0.1 to 1.0 ppm ^w / _v	high toxicity

(iii) Name: Aerofloat 208 Promoter

Company: Cyanamid

Chemistry: Sodium diethyl and sodium dissecondary butyl dithiophosphate.

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	1.0 to 10 ppm ^w /v	moderate toxicity

(iv) Name: Aerofloat 211 Promoter

Company: Cyanamid

Chemistry: Sodium di-isopropyl dithiophosphate

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	0.1 to 1.0 ppm ^w /v	high toxicity

(v) Name: Aerofloat 238 Promoter

Company: Cyanamid

Chemistry: Sodium di-secondary butyl dithiophosphate

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1,000 to 10,000 ppm ^w /v	relatively non-toxic

Toxicity (Provided by Cyanamid):

Median Tolerance Limit (96 hours) ppm

Trout	210
Salmon	152
Oysters	7.58
BOD (lb./lb.)	0.07 (Cyanamid value)
COD (lb./lb.)	1.28 (Cyanamid value)

(vi) Name: Aerofloat 243 Promoter

Company: Cyanamid

Chemistry: Sodium di-isopropyl dithiophosphate

Toxicity: Unknown

(vii) Name: Aerofloat 249 Promoter

Company: Cyanamid

Chemistry: Sodium di-amyl dithiophosphate

Toxicity: Unknown

(viii) Name: Aero Promoter 400 Series

Company: Cyanamid

Chemistry: mixtures of sulfhydryl type compounds.

Toxicity (OWRC Lab. value).

(a) Aero Promoter 404

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
D. Magna	10 to 100 ppm ^w /v	moderate toxicity
P. Promelas	1.8 to 18 ppm ^w /v	moderate toxicity

(b) Aero Promoter 407

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	3.2 to 32 ppm ^w /v	moderate toxicity

(c) Aero Promoter 412

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1.0 to 10 ppm ^w /v	moderate toxicity

(d) Aero Promoter 425

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	5.6 to 56 ppm ^w /v	moderate toxicity

(ix) Name: Aero Promoter 700 Series

Company: Cyanamid

Chemistry: Fatty acid type products of vegetable origin.

Toxicity (OWRC Lab. Value):

(a) Aero Promoter 710

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	10 to 100 ppm ^v /v	moderate toxicity

(b) Aero Promoter 723

Unknown

(c) Aero Promoter 765

Unknown

(x) Name: Aero Promoter 800 Series

Company: Cyanamid

Chemistry: Anionic sulphonate type collectors.

Toxicity (OWRC Lab. Value):

(a) Aero Promoter 801

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1.0 to 10 ppm ^v /v	moderate toxicity

(b) Aero Promoter 825

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	0.56 to 5.6 ppm ^w /v	high toxicity

(c) Aero Promoter 830

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	10 to 100 ppm ^w /v	moderate toxicity

(d) Aero Promoter 845

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	3.2 to 32 ppm ^v /v	moderate toxicity

(e) Aero Promoter 899

Unknown

(f) Aero Promoter 824

Unknown

(xi) Name: Aero Thiocarbanilide 130

Company: Cyanamid

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	32 to 320 ppm ^w /v	moderate toxicity

(xii) Name: Aero Promoter 3302
Aero Promoter 3461

Company: Cyanamid

Chemistry: Aero Promoter 3302 and its homolog 3461
are water-insoluble oily collectors.

Toxicity (OWRC Lab. Value):

(a) Aero Promoter 3302

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	5.6 to 56 ppm ^v /v	moderate toxicity

Toxicity (Provided by Cyanamid):

	<u>Median Tolerance Limit (96 hours) ppm</u>
Trout	1.5
Salmon	1.4
Oysters	0.68
BOD (lb./lb.)	0.16 (Cyanamid value)
COD (lb./lb.)	1.89 (Cyanamid value)

(b) Aero Promoter 3461

Unknown

(xiii) Name: Aero Promoter 3477
Aero Promoter 3501

Company: Cyanamid

Chemistry: Unknown

Toxicity (OWRC Lab. Value):

(a) Aero Promoter 3477

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	100 to 1,000 ppm ^w /v	relatively non-toxic

Toxicity (Provided by Cyanamid):

	<u>Median Tolerance Limit (96 hours) ppm</u>
Trout	159
Salmon	110
Oysters	1.11
BOD (lb./lb.)	0.05 (Cyanamid value)
COD (lb./lb.)	1.06 (Cyanamid value)

(b) Aero Promoter 3501

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1,000 to 10,000 ppm ^w /v	relatively non-toxic

Toxicity (Provided by Cyanamid):

	<u>Median Tolerance Limit (96 hours) ppm</u>
Trout	284
Salmon	225
Oysters	4.71
BOD (lb./lb.)	0.07 (Cyanamid value)
COD (lb./lb.)	1.09 (Cyanamid value)

(xiv) Name: Aeromine 3035 Promoter
Aeromine 3037 Promoter

Company: Cyanamid

Chemistry: Unknown. Cationic collectors.

Toxicity (OWRC Lab. Value):

(a) Aeromine 3037 Promoter

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	3.2 to 32 ppm ^w /v	moderate toxicity

(b) Aeromine 3035 Promoter

Unknown

(xv) Name: Z-200

Company: Dow

Chemistry: Isopropyl Ethylthionocarbamate

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	10 to 100 ppm ^v /v	moderate toxicity

(xvi) Name: Reagent S-3533

Company: Cyanamid

Chemistry: An emulsified form of Aero Promoter 3302.

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	0.1 to 1.0 ppm ^v /v	high toxicity

(xvii) Not available

(xviii) Name: Pamak 4
Pamak 6
Pamak LE

Company: Hercules

Chemistry: Tall oil fatty acids.

Pamak fatty acids consist primarily of acids containing 18 carbon atoms. Acids of this group are oleic, containing one double bond, and linoleic, containing two double bonds in both conjugated and nonconjugated positions.

Also present are small amounts of palmitic, a saturated 16-carbon acid, smaller amounts of stearic and margaric, and traces of C_{19} and C_{20} saturated and C_{20} unsaturated acids.

Formulas for the principal acids in Pamak are:

Oleic (9-octadecenoic)



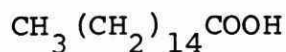
Linoleic, nonconjugated (9, 12-octadecadienoic)



Linoleic, conjugated (9, 11-octadecadienoic)



Palmitic (hexadecanoic)



The unsaponifiable matter in Pamak fatty acids is largely composed of decarboxylated fatty and resin acids,

sterols, ketones, and lactones.

Most of the resin acids present in Pamak are pimaric and secodehydroabietic, with lesser amounts of abietic, isopimaric, and closely related isomers.

Typical Properties (Pamak C4):

Rosin Acids, %	4.5
Fatty Acids, %	91.3
Unsaponifiabiles, %	4.2
Iodine Value	138-140

(xix) Name: AROSURF MG-83

Company: Ashland

Chemistry: Unknown. Cationic reagent. Water dispersible. A viscous amber liquid having a specific gravity (25°/25° C) of 0.925.

(xx) Name: AROSURF MG-98A

Company: Ashland

Chemistry: Unknown. Cationic reagent. Water dispersible. A viscous amber liquid having a specific gravity (25°/25° C) of 0.89.

(xxi) Other Products

(a) Company: Armour Hess (Britain)

General:

ARMEEN, ARMAC, DUOMEEN, DUOMAC, ARMOFLOTE, ARMACFLOTE and ETHOMEEN are registered trade marks of Armour Hess.

Armour Hess offer a wide selection of cationic collectors. The basis of these is nearly always an aliphatic amine (ARMEEN) or an aliphatic diamine (DUOMEEN). Products such as ARMACS, DUOMACS, (fully neutralized acetates of the ARMEENS and DUOMEENS), ARMOFLOTES and ARMACFLOTES are also available.

The ARMEENS and DUOMEENS are not added directly to the ore-water pulp due to their insolubility in water but are most commonly used in the form of their partially or fully neutralized acetate salts (ARMACS) or as their hydrochlorides. These salts are usually prepared in situ or in emulsified form. ARMEENS can be used as such if they are first dissolved in a solvent, for example, in an auxiliary collector such as a hydrocarbon oil or in a frothing agent such as pine oil. Choice of the solvent is dependent upon the particular mineral to be floated; for example in the flotation of silica from phosphate an excessive amount of kerosene

could adversely affect the flotation so an alcohol frother or pine oil may be preferred as solvent for the ARMEEN.

The flotation mills which purchase ARMEENS and DUOMEENS often prepare the water soluble salts in situ.

ARMOFLOTES and ARMACFLOTES are tailor made ready-to-use cationic collectors for specific ores. The ARMOFLOTES are preferentially oil soluble and are incorporated into an auxiliary collector such as kerosene or in a frother such as pine oil. The ARMACFLOTES are partially or fully neutralized ARMOFLOTES and are thus water soluble.

The concentration of Armour Hess collectors required in flotation is low and it is essential that the correct concentration is not exceeded. Cationic collectors function because they have a higher affinity for one particular mineral in a system; if an excess of collector is added, minerals other than the ones required may be floated causing a reduction in collector selectivity. Even if the system is such that selectivity would not be impaired, excess of collector can produce a "double-layer collector effect"; the second layer is orientated with the hydrophilic group away from the mineral, which retards the flotation, depresses the

mineral in the initial cells and results in decreased recovery, possible loss of selectivity and an increase in the circulating load.

PRINCIPAL PROPERTIES OF PRIMARY "ARMEENS"

"Armeen"	18D	C	CD	S	SD	T	TD	HT	HTD	2HT
<u>Typical Analysis</u>										
Iodine Value	3	12	12	70	70	43	43	5	5	4
Primary Amine %	99	95	99	95	99	95	99	95	99	5
Secondary & Tertiary Amine %	1	5	1	5	1	5	1	5	1	92
Colour, Gardner	2	10	2	10	2	10	2	8	2	3
Moisture %	1	1	1	1	1	1	1	1	1	1
Ave. Combining Weight	278	210	204	282	270	270	265	272	267	500
<u>Physical Properties</u>										
Physical Form @ 25°C	Solid	Liquid	Liquid	Paste (+ Liquid)	Soft paste	Paste	Paste	Solid	Solid	Solid
Flash Point	300°F	240°F	230°F	315°F	305°F	315°F	305°F	320°F	315°F	435°F
Cleveland Open Cup	149°C	116°C	110°C	157°C	152°C	157°C	152°C	160°C	157°C	224°C
Fire Point	350°F	270°F	250°F	355°F	345°F	355°F	345°F	365°F	360°F	480°F
Cleveland Open Cup	172°C	132°C	121°C	179°C	174°C	179°C	174°C	185°C	182°C	249°C
Melting Point °F	121-132	53-59	56-62	80-85	80-85	92-104	89-100	117-131	117-131	140-148
A.S.T.M. °C	49-56	11-15	13-17	26-29	26-29	35-40	31-38	47-55	47-55	60-64
<u>Specific Gravity</u>										
(Reference water at 25°C)	--	0.805	0.804	--	--	--	--	--	--	--
(Reference water at 4°C)	70°C 0.784	0.774	0.773	0.790	0.789	0.791	0.790	0.791	0.790	0.791
<u>Viscosity</u>										
Saybolt Seconds	35°C --	44.2	43.0	46.3	46.2	47.0	45.2	--	--	--
Universal	75°C 39.9	33.6	32.8	--	--	37.8	37.4	38.8	36.3	58.0

PRINCIPAL PROPERTIES OF "DUOMEENS"

"Duomeen"	T	C
<u>Typical Analysis</u>		
Iodine Value	38	9
Duomeen Activity %	89	89
Colour, Gardner	14	14
Moisture %	1.0	1.0
Molecular Combining Weight	360	290
<u>Physical Properties</u>		
Physical Properties at 25°C	Heavy Paste	Liquid
Melting Point	111-118°F 44-48°C	68-75°F 20-24°C
<u>Specific Gravity</u>		
(Reference water @ 25°C)		
40°C	--	0.824
70°C	0.813	0.803
<u>Viscosity</u>		
cps		
25°C	880	10
35°C	10	--

SOLUBILITY OF "ARMACS" AND "DUOMACS" IN WATER

(grams Armac or Duomac in 100 grams of water)

Temperature ($^{\circ}\text{C}$)	0	20	40	60	80	100
Armac C	27.0	29.5	47.5	49.5	52.0	55.0
Armac T	0.1	11.0	12.0	13.0	14.0	15.0
Armac HT	0.1	0.1	9.0	10.0	11.5	13.0
Duomac C	Duomacs are fairly soluble in water at room temperature and below, but at 15-30% concentrations, gels tend to form, especially at temperatures from 30°C upwards.					
Duomac T						

NOTE: The distilled grades of the above products (e.g., ARMAC CD is distilled, ARMAC C is not distilled) can be expected to have a solubility of the same order of magnitude as the undistilled grades.

PHYSICAL CHARACTERISTICS OF "ARMOFLOTE" AND "ARMACFLOTE"
FLOTATION COLLECTORS

	<u>Melting point</u> <u>Degrees F</u>	<u>Appearance at 77°F</u> <u>(25°C)</u>	<u>Colour</u>
Armoflote A-101	80-85	Semi-fluid to soft paste	Brown
Armoflote A-104	63-70	Liquid	Amber
Armoflote A-106	100-105	Soft solid	Light Brown
Armoflote A-252	70-75	Liquid	Dark Brown
Armoflote P	91-96	Soft paste	Dark Brown
Armacflote A-101	110-120	Soft paste	Brown
Armacflote A-103	60-65	Liquid	Dark Reddish Brown
Armacflote A-104	70-80	Liquid to soft paste	Light Tan
Armacflote A-252	117-127	Solid	Dark Brown
Armacflote P	97-98	Soft paste	Dark Brown
Armacflote P-35	110-110	Soft paste	Dark Brown

(b) Company: Hoechst (Germany)

General:

Aromatic and Aliphatic Dithiophosphoric Acid Esters

Phosocresol Brands

Phosocresol A

Phosocresol B

Phosocresol C

Phosocresol E

Phosocresol F

All phosocresol brands are liquid products combining collecting and frothing properties (collectors/frothers). The collecting components are aromatic, mainly dixylenyl resp. dicresyl dithiophosphoric acids. The collecting effect increases from Phosocresol A to C and from E to F, while the frothing effect increases in the reverse order.

Phosocresol A, B and C are virtually immiscible with water and must be fed in its original form.

Phosocresol E and F are miscible with water in any ratio and can therefore be used as dilute aqueous solutions. Consequently, they are especially suitable for the

highly selective flotation of low metal contents or for use in small flotation plants. While Phosocresol brands are used for purposes similar to those for xanthates, they have a more selective action, collecting Cu, Pb, Sb and Co sulphide minerals very effectively while collecting hardly any Fe sulphides (pyrite, marcasite, pyrrhotite, arsenopyrite).

Collector Hoe F 1/493

Collector Hoe F 3/10

Collector Hoe F 1559

Collector Hoe F 1578

Collector Hoe F 1579

Sodium dialkyl dithiophosphates with various alkyl chains. The products in powder form are readily soluble in water and used chiefly in the flotation of sulphide and oxide Cu minerals, and of sphalerite, stibnite, and cobalt minerals. Like the aromatic dithiophosphoric acids (see Phosocresol brands), they collect Fe sulphide minerals far less effectively than do xanthates.

Various Test Products

Collector Hoe F 1/432

Collector Hoe F 1/433

Collector Hoe F 1/434

Collector Hoe F 1/438

Suitable as collectors for sulphide minerals either separately or together with xanthates or dithiophosphates, which they sometimes greatly exceed in activity. They belong to various classes of chemical compounds. Hoe F 1/432 is a powder readily soluble in water, and therefore this product is best used as a diluted aqueous solution. The other products are oily liquids which must be used undiluted because they are not miscible with water.

Collectors for the Flotation of Oxide Minerals and Salts

(i) Cationic Collectors

Flotigam Brands

Flotigam P and PA (coconut fatty amine)

Flotigam S and SA (stearylamine)

Flotigam T and TA (tallow fatty amine)

Primary amines and their acetates (indicated by the letter A) particularly suitable for the flotation of potassium

salts. They are also used as collectors for sulphidized (Na_2S , NaHS) oxide Zn minerals (zinc carbonate) and for quartz and acidic silicate minerals (e.g., mica, feldspar).

Amine Hoe F 2/286

Tallow fatty propylene diamine diacetate, particularly suitable for collecting quartz.

Amine Hoe F 1/403-1

Amine Hoe F 1/403-2

Amine Hoe F 1/403-3

Special formulations fully liquid at room temperature and therefore very easily handled; they should be applied undiluted in the flotation pulp. They are used in rapid flotation, especially for zinc carbonate and quartz (e.g., in reverse iron ore flotation).

(ii) Anionic Collectors

p-tolyl arsonic acid (PTA)

A highly specialized and selective collector for cassiterite.

Medialan KA conc.

Medialan A conc.

Hostapon CT paste

Hostapon T powder

Product 1175 (alkane sulphonate)

Alkyl phosphoric acid Hoe F 1/415 etc.

Emulsogen STH

Depending on the type, these products are collectors for:

oxide minerals such as hematite, magnetite, rutile, ilmenite, chromite, etc;

phosphate minerals such as apatite, phosphorite and monazite;

fluorite, baryte and celestite;

uranium minerals;

silicate minerals such as pyroxenes, amphiboles, zircon, beryl and kyanite;

scheelite, wolframite

and numerous other minerals.

Some of these products may also be used as anionic emulsifiers for fatty acids (oleic acid, tall oil fatty

acids), greatly increasing their flotation activity.

Collectors/Frothers for Coal Flotation

Montanol 300 Brands

Hoechst coal flotation agents are based on Montanol 300, a special mixture of higher alcohols; various additives are used according to the required purpose. All Hoechst coal flotation agents are free of phenols or other components undesirable in the effluent.

MODIFYING (REGULATING) AGENTS

Chemical products which are used to modify or control the normal behavior of minerals in a flotation operation are broadly classed as modifying (regulating) agents. The list of modifying agents used in flotation is long and varied and generally includes all reagents whose principal function is neither collecting nor frothing.

(A) pH Modifiers

Most, if not all, flotation operations in the Province of Ontario are carried out using alkaline or near-neutral circuits. In the majority of flotation operations, there is usually a given pH range in which optimum results

are obtainable.

Sulphide flotation circuits do not have to be alkaline before flotation can take place. In fact, the floatability of sulphides is often enhanced in a low pH (or acid) pulp. However, selectivity may be hampered by the introduction of cation activators resulting from reactive minerals dissolving in the acid system. Higher pH--more alkaline--pulp commonly permit good flotation with greater selectivity and less corrosion of equipment.

The alkalinity regulators most commonly employed in the flotation circuits in the Province are as follows:

(a) Slaked Lime ($\text{Ca}(\text{OH})_2$)

Because of its low cost, lime is used in substantially all flotation circuits where the calcium ion is not objectionable (this includes most copper and zinc flotation circuits). Some minerals, notably pyrite and to a lesser extent galena, have a tendency to adsorb calcium ions in preference to the collector and, as a result, are less readily floatable in a pulp containing lime.

This difficulty is eliminated by the use of soda ash which precipitates naturally occurring calcium ions

and also provides the necessary alkalinity.

(b) Sodium Carbonate (Na_2CO_3) ('soda ash')

(c) Sodium Hydroxide (NaOH) ('caustic soda')

Acid pH control is usually obtained with sulphuric acid (H_2SO_4) because of its low cost.

Toxicity data concerning all of the above reagents are given in the section of this report dealing with 'bulk' chemicals.

(B) Activating Agents

This class of reagents is added to a flotation system to permit better collector attachment to the mineral to be floated. The classic example of an activating agent is the addition of copper sulphate to a flotation pulp containing sphalerite (ZnS). The cupric ion attaches to the sphalerite, allowing the mineral to be floated with a xanthate. Such flotation is not possible with a short-chain xanthate in the absence of an activating agent. The activation of sphalerite with copper, lead, or silver is a chemical reaction in which the Cu^{2+} , Pb^{2+} , or Ag^+ ions replace zinc in the sphalerite lattice through the formation of a more insoluble sulphide. In the case of copper activation, the exchange

occurs rapidly until three layers of Zn^{2+} have been replaced and then continues more slowly.

Another widely used activation process is that of calcium activation of quartz. Since quartz is generally negatively charged, it may be readily floated with a cationic collector. However, if metal ions such as Al^{3+} , Ba^{2+} , Ca^{2+} , Cu^{2+} , Fe^{3+} , Pb^{2+} , etc., are added, the quartz may be floated with an anionic collector. For economic reasons, lime and crude oleic acid (tall oil) are ordinarily used in this form of quartz flotation.

One further form of activation is sulfidizing. In 1905, Schwarz patented the use of sodium sulphide to aid in the flotation of oxidized copper and lead ores. The reasons for its effectiveness are still not known, though it is probably connected with the formation of a new mineral surface simulating that of the metal sulphide. After sulfidizing, the oxidized mineral is floated with a xanthate or similar collector.

As stated above, the outstanding example of an activating agent is copper sulphate which is used to activate sphalerite and marmatite, the iron sulphides, and in some

cases arsenopyrite. Other examples include hydrogen or sodium sulphide to float lead and copper carbonate minerals; lead nitrate to improve the flotation of various non-metallic minerals with promoters of the fatty acid type; use of aluminum chloride for the flotation of mica with cationic type promoters; and cyanide to improve recovery of weathered or slimy zinc minerals.

Toxicity of Specific Activating Agents

(i) , Copper Sulphate (CuSO_4 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

Toxicity:

The toxicity of copper sulphate to fish varies with the species and exposure period, and the physical and chemical characteristics of the water. Goldfish have been reported to have been killed by as little as 0.002 mg/litre (a), and yet they have survived concentrations of one mg/litre in hard water for at least the three-day period of study (b). Anderson (c) gives 0.016 mg/litre as the toxic threshold of copper sulphate for sticklebacks in tap water. Hale (d) and Hopkins (e) have found 0.14 to 2.0 mg/litre to be limiting safe concentrations for many different kinds of fish. Briefly summarizing the data from numerous papers,

concentrations from 0.002 mg/litre to 200 mg/litre or more have been reported lethal to various fish in different waters.

The highest concentrations of copper sulphate tolerated by specific fish have been reported (f, g, h, i, j, k, l) as follows:

<u>Fish</u>	<u>Concentration in mg/litre</u>
Trout	0.14
Carp	0.33
Suckers	0.33
Catfish	0.40
Pickereel	0.40
Goldfish	0.5
Perch	0.67
Black bass and Bluegills	0.8
Sunfish	1.35
Black bass	2.00

Wallen et al. (m) studied the toxicity of pure chemicals to the mosquito-fish (*Gambusia affinis*) in highly turbid waters. At temperatures of 24-27°C, the 96-hour TL_m for copper sulphate was 75 mg/litre. Furthermore, high concentrations of this chemical lowered the turbidity from 750 mg/litre to less than 25 mg/litre.

Fish have been more resistant to copper sulphate in hard, alkaline waters than in soft, acid waters (n, o, p, q, r, s, t). Indeed, toward rainbow trout at 17-18°C, copper

sulphate was found to be about ten times more toxic in soft water (12 mg/litre as CaCO_3) (u). The sulphates of copper and zinc and those of copper and cadmium are synergistic in their toxic effect upon fish (v). On the other hand, sodium nitrite has an antagonistic effect on the toxicity of copper sulphate to goldfish; 5000 mg/litre of sodium nitrite has decreased the toxic effect of 10 mg/litre of copper sulphate, and the addition of 50 mg/litre of sodium chloride has still further reduced it (w). Sodium nitrate has also been reported to have antagonistic action against copper sulphate (x).

Turnbull et al. (y) studied the toxic effect of copper sulphate toward bluegill sunfish at 20°C using a synthetic test water containing 172 mg/litre of dissolved solids, 101.2 mg/litre of hardness (as CaCO_3), 72.0 mg/litre of alkalinity (as CaCO_3), and pH 8.3. Similar tests were conducted in waters approximately twice and half as mineralized as the standard water. They found the 48-hour TL_m to be 7.0 mg/litre of copper sulphate with the standard test water, only 3.0 mg/litre in the half-strength water, but 44 mg/litre in the double-strength water.

Among other aquatic fauna, Chironomus larvae have not been harmed by copper sulphate in concentrations of 5.0 mg/litre (z) and 100 mg/litre (aa, ab); Polycelis nigra has been killed in 48 hours in lake water by 0.47 mg/litre (ac, ad); Daphnia magna has been killed by 0.096 mg/litre (ae); 0.01 to 0.02 mg/litre (af, ag), and 0.08 mg/litre (ah); and planarian worms have been killed by 1.0 mg/litre (ai). The addition of 1.0 mg/litre of copper sulphate to a culture medium completely inhibited the growth of Sphaerotilus (aj).

The following rates of application of copper sulphate have been recommended (ak) to control specific types of algae in farm ponds:

Anabaena	0.09 mg/litre
Beggiatoa	5.0 mg/litre
Chara	0.2-5.0 mg/litre
Cladophora	1.0 mg/litre
Cladothrix	0.2 mg/litre
Conferva	0.4 mg/litre
Navicula	0.07 mg/litre
Oscillatoria	0.1-0.4 mg/litre
Scenedesmus	5.0-10.0 mg/litre
Spirogyra	0.05-0.3 mg/litre
Ulothrix	0.2 mg/litre
Volvox	0.25 mg/litre

- (a) Jones, J.R.E., "The Relative Toxicity of Salts of Lead, Zinc and Copper to the Stickleback", Jour. Expt. Biol. (1938).

- (b) Anderson, B.G., "The Apparent Thresholds of Toxicity of *Daphnia magna* for Chlorides of Various Metals When Added to Lake Erie Water", Trans. Amer. Fish. Soc. (1948); Water Pollution Abs. (1950).
- (c) See (b) above.
- (d) Hale, F.E., "The Use of Copper Sulphate in Control of Microscopic Organisms", Phelps Dodge Refining Corp. (1950).
- (e) Hopkins, E.S., "Water Purification Control", 2nd Ed., Williams and Wilkins (1936).
- (f) See (e) above.
- (g) See (d) above.
- (h) Derby, R.L. and Graham, D.W., "Control of Aquatic Growths in Reservoirs by Copper Sulphate and Secondary Effects of Such Treatment", Proc. A.S.C.E. (1953).
- (i) Hale, F.E., "Control of Algae", Water and Sewage Works (1952).
- (j) Gainey, P.L., and Lord, T.H., "Microbiology of Water and Sewage", Prentice-Hall Inc., N.Y. (1952).
- (k) Symons, G.E., "Tastes and Odour Control", Water and Sewage Works (1956).
- (l) Maguire, J.J., "Biological Fouling in Recirculating Cooling Water Systems", Ind. & Chem. (1956).
- (m) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (n) Hale, F.E., "Relation of Copper and Brass Pipe to Health", Water Works Eng. (1942).

- (o) Warrick, L.F., "The Wisconsin Committee on Water Pollution", Health Bull. Wisc. St. Bd. of Health (1949); Pub. Health Engineering Abs. (1951).
- (p) Anon., "Copper Sulphate for Aquatic Nuisances", Pub. Works (1942); Pub. Health Engineering Abs. (1943).
- (q) Warrick, L.F., Wirth, H.E., and Van Horn, W., "Control of Micro-Organisms and Aquatic Vegetation", Water Works and Sewerage (1944); Pub. Health Engineering Abs. (1945).
- (r) Domogolla, B., "Scientific Studies and Chemical Treatment of the Madison Lakes", A Symposium on Hydrobiology, Univ. of Wisconsin (1941).
- (s) Warrick, L.F., "Chemical Control of Water Weeds", Eng. News-Record (1940); Water Pollution Abs. (1940).
- (t) Anon., "The Sensitivity of Aquatic Life to Certain Chemicals Commonly Found in Industrial Wastes", Acad. of Natural Sciences, Philadelphia (1960).
- (u) Anon., "Report of the Water Pollution Research Board, With the Report of the Director of the Water Pollution Research Laboratory for the Year 1959", Dept. of Scientific and Ind. Res., H.M. Stationery Office, London (1960).
- (v) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee", Report No. 3 (1950).
- (w) Cole, A.E., "The Effects of Pollutational Wastes on Fish Life", A Symposium on Hydrobiology, Univ. of Wisconsin (1941).
- (x) See (v) above.
- (y) Turnbull, H., DeMann, J.G., and Weston, R.F., "Toxicity of Various Refinery Materials to Fresh Water Fish", Symposium on Waste Disposal in the Petroleum Industry, Ind. Eng. Chem. (1954).

- (z) Buchmann, W., "Chironomous Control in Bathing Establishments, Swimming Pools, and Water Supplies by Means of Chlorine and Copper", Jour. A.W.W.A. (1933).
- (aa) Brown, K.W., "Experiences with Blood Worms in an Uncovered Reservoir", Water Works Engineering (1932); Water Pollution Abs. (1933).
- (ab) Bachmann, H., Birrer, A., and Weber, H., "The Poisonous Effect of Chemical Substances on Lower Water Organisms", Z. Hydrol. (Zurich) (1933); Water Pollution Abs. (1936).
- (ac) See (v) above.
- (ad) Jones, J.R.E., "A Further Study of the Relation Between Toxicity and Solution Pressure, With Polycelis nigra as Test Animal", Jour. Exp. Biol. (1940).
- (ae) See (v) above.
- (af) See (a) above.
- (ag) See (b) above.
- (ah) Anderson, B.G., "The Toxicity Thresholds of Various Substances Found in Industrial Wastes as Determined by the Use of Daphnia magna", Sewage Works Jour. (1944).
- (ai) See (a) above.
- (aj) Waitz, S., and Lackey, J.B., "Morphological and Biochemical Studies on the Organism Spaeerotilus natans", Engineering Progress Univ. Florida Leaflet No. 114 (1959); Quarterly Jour. of Florida Acad. of Science (1959).
- (ak) Anon., "The Destruction of Algae in Farm Ponds and Other Bodies of Water", U.S.D.A. Bureau of Plant Industry, Soils and Agricultural Engineering, Bull. 77CC (1954).

NOTE: A typical commercial specification for copper sulphate salt is as follows:

Cu	25%
Pb	0.006%
Sb	0.003%
Co	0.02%
Ni	0.02%
Fe	0.19%
Zn	0.06%
Cl	0.015%
As	0.01%
Water insoluble	0.007%

(ii) Sodium Sulphide (Na_2S)

The following concentrations of sodium sulphide have been reported as toxic or lethal to fish:

<u>Concentration in mg/litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
0.55	pH 5.2	--	Young carp	a
1.0 (threshold)	Aerated	--	Salmonoid fish	b
1.8 (lethal)	Aerated	--	Salmonoid fish	c
2.0	Distilled	--	Minnows	d
2.4	--	--	Brown trout	e
3.0	--	--	Minnows	f
3.0	12°C	--	Cutthroat trout	g
3.0	--	--	Shiners, Minnows	h, i, j

<u>Concentration in mg/litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
3.1	15°C	--	Silver salmon	k
3.2	--	48-hour TL _m	Fathead minnows	l
3.3	pH 7.4	--	Young carp	m
3.5	17.5°C	--	King salmon	n
7.8	--	90 minutes	Minnows	o
10-11	Hard, 15°C	6 hours	Minnows	p
11	--	--	Stickleback	σ
12-13	Distilled, 25°C	6 hours	Minnows	r
39	--	6 minutes	Minnows	s
50	Hard	--	Minnows	t
61	Standard	48-hour TL _m	Bluegill sunfish	u
750	Turbid	96-hour TL _m	Mosquito- fish	v

The maximum concentration of sodium sulphide that produced no mortality has been given (w) as 1.8 mg/litre for king salmon at 17.5°C, 1.3 mg/litre for silver salmon at 15°C, and 1.0 mg/litre for cutthroat trout at 12°C. Fish tried to avoid solutions of sodium sulphide in concentrations of 3.1 to 39.0 mg/litre (x).

Fish removed from toxic concentrations of sodium sulphide before they stopped breathing recovered and survived (y). Minnows exposed to 17.1 mg/litre of sodium sulphide in tap water have been disturbed for as long as five

hours; within 24 hours, however, the sulphide had disappeared and the fish recovered (z). On the other hand, Ellis quotes a reference to the effect that exposure for one hour to 1150 mg/litre of sodium sulphide in tap water has resulted in the death of tench six days later (aa).

When Na_2S is added to water, it dissociates to release sulphide ions which then react with hydrogen ions to form HS^- or H_2S , depending on the pH value of the solution. For that reason, the toxicity of sodium sulphide tends to increase as the pH of the water decreases from 9 to 6 (ab). This relationship has been shown by Tomiyama and Yamagawa (ac) for young carp as follows:

<u>pH Value</u>	<u>Critical Lethal Concentration, mg/litre</u>
5.2	0.55
6.1	0.95
7.4	3.3
8.2	8.0

Other aquatic life have responded to sodium sulphide as shown below:

<u>Concentration in mg/litre</u>	<u>Organism</u>	<u>Remarks</u>	<u>Refer- ence</u>
1-2	Mayfly larvae	Killed	ad
2-1000	Insect larvae	Killed	ae
2.44	Bivalve larvae	Lethal	af
3.2	Mesocyclops leuckarti	Toxic threshold	ag
9.4-10	Daphnia magna	Killed or immobilized	ah ai aj
10	Daphnia magna	48-hour MLD at 17°C	ak
34	Polycelis nigra	Toxic threshold	al
63	Daphnia	Toxic threshold	am
97	Scenedesmus	Toxic threshold	an
226	E. coli	Toxic threshold	ao
1000	Chironomus larvae	Resisted	ap

- (a) Tomiyama, T., and Yamagawa, A., "The Effect of pH Upon Toxic Effects of Sulphide and of Sulphite on Young Carp", Bull. Jap. Soc. Sci. Fish. (1950); Water Pollution Abs. (1953).
- (b) Haydu, E.P., Amberg, H.R., and Dimick, R.E., "The Effect of Kraft Mill Waste Components on Certain Salmonoid Fishes of the Pacific Northwest", TAPPI (1952); Water Pollution Abs. (1953).
- (c) See (b) above.
- (d) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Toxic Components to Fish", Sewage and Industrial Wastes (1950).
- (e) Jones, J.R.E., "Fish and River Pollution", Chapter 7 of "Aspects of River Pollution", L. Klein, Editor, Butterworth Scientific Publ., London (1957).
- (f) Anon., "The Toxicity of Kraft Pulping Wastes to Important Fish Food Species of Insect Larvae", Nat'l Council for Stream Improvement Tech. Bull. (1949).

- (g) Haydu, E.P., Amberg, H.R., and Dimick, R.E., "The Effect of Kraft Mill Waste Components on Certain Salmonoid Fishes of the Pacific Northwest", Tech. Assoc. Pulp and Paper Ind. (1962).
- (h) Gehm, H.W., "The Toxic Effects of Sulphate Pulp Waste Liquors on Fish and Other Aquatic Life", National Council for Stream Improvement, Tech. Bull. (1945).
- (i) Anon., "A Study of the Toxic Components of the Waste Waters of Five Typical Kraft Mills", National Council for Stream Improvement, Tech. Bull. (1948).
- (j) See (f) above.
- (k) See (g) above.
- (l) Black, H.H., McDermott, G.N., Henderson, C., Moore, W.A., and Pahren, H.R., "Industrial Waste Guide, By-Product Coke", Proc. 11th Industrial Waste Conf., Purdue University (1957).
- (m) See (a) above.
- (n) See (g) above.
- (o) Jones, J.R.E., "The Oxygen Consumption of *Gasterosteus aculeatus* L. in Toxic Solutions", Jour. Exp. Biol. (1947); Water Pollution Abs. (1947).
- (p) LeClerc, E., "The Self-Purification of Streams and the Relationship Between Chemical and Biological Tests", Proc. of the 2nd Symposium on the Treatment of Waste Waters, Pergamon Press, London (1960).
- (q) See (e) above.
- (r) See (p) above.
- (s) See (o) above.
- (t) See (d) above.

- (u) Turnbull, H., DeMann, J.G., and Weston, R.F., "Toxicity of Various Refinery Materials to Fresh Water Fish", Symposium on Waste Disposal in the Petroleum Industry, Ind. Eng. Chem. (1954).
- (v) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (w) See (g) above.
- (x) Jones, J.R.E., "A Further Study of the Reactions of Fish to Toxic Solutions", Jour. Exp. Biol. (1948).
- (y) See (o) above.
- (z) Schaut, G.G., "Fish Catastrophes During Drought", Jour. A.W.W.A. (1939).
- (aa) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (ab) See (x) above.
- (ac) See (a) above.
- (ad) See (f) above.
- (ae) See (f) above.
- (af) Woelke, C.E., "Bioassay - The Bivalve Larvae Tool, Proceedings of the Tenth Pacific Northwest Symposium on Water Pollution Research, "Toxicity in the Aquatic Environment", Portland, Ore. (1961).
- (ag) Anderson, B.G., Chandler, D.C., Andrews, T.F., and Jahoda, W.J., "The Evaluation of Aquatic Invertebrates as Assay Organisms for the Determination of the Toxicity of Industrial Wastes", Amer. Petroleum Inst. Project Final Report (1948).

- (ah) Anderson, B.G., "The Toxicity Thresholds of Various Sodium Salts Determined by the Use of *Daphnia magna*", Sewage Works Jour. (1946).
- (ai) See (f) above.
- (aj) See (ag) above.
- (ak) Anon., "The Toxicity of Kraft Pulping Wastes to Typical Fish Food Organisms", Tech. Bull. National Council for Stream Improvement (1947).
- (al) Jones, J.R.E., "A Study in the Relative Toxicity of Anions With *Polycelis nigra* (Planarian) as Test Animal", Jour. Exp. Biol. (1941).
- (am) Bringmann, G., and Kuhn, R., "The Toxic Effects of Waste Water on Aquatic Bacteria, Algae, and Small Crustaceans", Gesundheits-Ing. (1959).
- (an) See (am) above.
- (ao) See (am) above.
- (ap) See (f) above.

(iii) Lead Nitrate $\text{Pb}(\text{NO}_3)_2$

Toxicity:

For tadpoles in tap water, 1.6 mg/litre of lead nitrate is deleterious to growth and 3.3 mg/litre is lethal (a). Fish appeared to try to avoid, i.e., react negatively, to solutions of lead nitrate varying in strength from 0.33 to 644 mg/litre but reacted positively to a 6640 mg/litre solution after a temporary initial negative reaction (b).

Westfall found that concentration of dissolved oxygen has a significant effect on the response of goldfish to lead nitrate; for example, all the fish tested survived a 2-hour exposure to 5 mg/litre of lead nitrate in the presence of 6.2 mg/litre of oxygen, but all the fish tested died within 2 hours in the presence of only 1.4 mg/litre of dissolved oxygen (c).

In fresh water, 3 mg/litre lead nitrate has been fatal to *Fundulus* within 12 hours (d). Using lead nitrate, Jones found the lethal concentration limit of lead for sticklebacks to be 0.1 mg/litre. At different concentrations of lead, the average survival times of the fish were as follows: one day at 1.0 mg/litre, two days at 0.7 mg/litre, four days at 0.3 mg/litre, and one week at 0.2 mg/litre (e). However, goldfish died only after an 80-hour exposure to 63 mg/litre of lead (f). Minnows died within 48 hours when exposed to 0.4 mg/litre of lead in a solution of lead nitrate in non-toxic distilled water (g).

The following concentrations of lead nitrate have been reported to have killed fish:

Concentration of Lead Nitrate, in mg/litre	Type of <u>Water</u>	Time of <u>Exposure</u>	Type of <u>Fish</u>	<u>Reference</u>
0.16	Tap	--	Stickleback	h, i
0.53	Tap	--	Minnows, Sticklebacks and Brown trout	j
10	Natural	2.5 hours	Trout	k, l
10	Tap	24 and 48-hour TL ^m	Bluegill sunfish	m
10	Hard	4 days ^m	Goldfish	n
16	Tap	--	Goldfish	o
16.6	--	20 hours	Minnows	p
100	Hard	80 hours	Goldfish	q
165	Distilled	--	Fish	r
240	Highly turbid	96-hour TL ^m	Mosquito-fish	s
250	Distilled	4-5 days	Goldfish	t
250	Distilled	2-3 hours	Minnows	u
830	--	3 hours	Minnows	v
3320	--	2.2 hours	Minnows	w
8300	--	1.5 hours	Minnows	x
16600	--	1.4 hours	Minnows	y, z
44000	--	44 minutes	Minnows	aa
53000	--	40 minutes	Minnows	ab

On the other hand, 10 mg/litre of lead nitrate in hard water has not harmed fish during a 96-hour exposure period (ac).

Bringman and Kuhn (ad, ae) tested the effects of lead nitrate in River Havel water at pH 7.5 and a temperature of 24°C against several organisms during an exposure of 4 days. The threshold concentrations for deleterious action were as follows:

<u>Test Organism</u>	<u>Threshold Concentration in mg/litre of Lead</u>
Daphnia magna	5.0
Scenedesmus	2.5
Escherichia coli	1.3
Microregma	1.25

Cleland (af) found that lead nitrate in a concentration of about 200 mg/litre in sea water produced abnormalities in the eggs of sea urchins.

- (a) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (b) Jones, J.R.E., "A Further Study of the Reactions of Fish to Toxic Solutions", Jour. Exp. Biol. (1948).
- (c) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals as Salts", Sewage and Industrial Wastes (1953).
- (d) See (c) above.
- (e) Murdock, H.R., "Industrial Wastes. Some Data on Toxicity of Metals in Wastes to Fish Life are Presented", Ind. Eng. Chem. (1953).
- (f) Rudolfs, W., et al., "Industrial Wastes", Reinhold Publ. Co., N.Y. (1953).
- (g) See (c) above.
- (h) Jones, J.R.E., "Fish and River Pollution", Chapter 7 of "Aspects of River Pollution", L. Klein, Editor, Butterworth Scientific Publ., London (1957).

- (i) Anderson, B.G., "The Apparent Thresholds of Toxicity of *Daphnia magna* for Chlorides of Various Metals When Added to Lake Erie Water", Trans. Amer. Fish. Soc. (1948); Water Pollution Abs. (1950).
- (j) See (h) above.
- (k) See (a) above.
- (l) See (i) above.
- (m) Turnbull, H., DeMann, J.G., and Weston, R.F., "Toxicity of Various Refinery Materials to Fresh Water Fish", Symposium on Waste Disposal in the Petroleum Industry, Ind. Eng. Chem. (1954).
- (n) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee Report (1950).
- (o) See (h) above.
- (p) See (n) above.
- (q) See (a) above.
- (r) See (a) above.
- (s) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (t) See (a) above.
- (u) See (a) above.
- (v) Carpenter, K.E., "The Lethal Action of Soluble Metallic Salts on Fishes", Brit. Jour. Exp. Biol. (1927).
- (w) See (v) above.
- (x) See (v) above.

- (y) See (v) above.
- (z) Carpenter, K.E., "Further Researches on the Action of Metallic Salts on Fishes", Jour. Exp. Zool. (1930).
- (aa) See (z) above.
- (ab) See (z) above.
- (ac) See (a) above.
- (ad) Bringmann, G., and Kuhn, R., "The Toxic Effects of Waste Water on Aquatic Bacteria, Algae, and Small Crustaceans", Gesundheits-Ing. (1959).
- (ae) Bringmann, G., and Kuhn, R., "Water Toxicology Studies with Protozoans as Test Organisms", Gesundheits-Ing. (1959).
- (af) Cleland, K.W., "Heavy Metals, Fertilization and Cleavage in Eggs of *Psammochinus miliavis*", Exp. Cell. Research (1953).

(iv) Lead Acetate $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$

Toxicity:

Dawson (a) found evidence of injury to blood cells of catfish exposed for 16 to 183 days to a 50 mg/litre solution of lead acetate (27 mg/litre of Pb) in tap water, renewed at 48-hour intervals. Minnows were killed in 26 to 48 hours by 0.4 mg/litre of lead in a solution of lead acetate in non-toxic distilled water, renewed at regular intervals during the observation period.

It has been reported that lead acetate concentrations of 10 mg/litre in stream water killed trout (b, c, d). In distilled water, 5.0 mg/litre of lead acetate killed minnows in 4 to 16 hours; and 10 mg/litre in distilled water renewed every second day, killed goldfish in 12 days (e). The Washington Department of Fisheries (f) reported that lead acetate at a concentration of 2.8 mg/litre of lead killed fish in fresh water; but Fujiya (g) maintained that long-term exposure of carp to a much lower concentration of lead acetate (1.0 mg/litre as Pb) resulted in a harmful effect to their serum.

- (a) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts", Sewage and Industrial Wastes (1953).
- (b) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (c) Anderson, B.G., "The Apparent Thresholds of Toxicity of *Daphnia magna* for Chlorides of Various Metals When Added to Lake Erie Water", Trans. Amer. Fish. Soc. (1948); Water Pollution Abs. (1950).
- (d) Ellis, M.M., "Pollution of the Coeur d'Alene River and Adjacent Waters by Mine Wastes", U.S. Bur. Fish. Spec. Sci. Rept. (1940).
- (e) See (b) above.

- (f) Gooding, D., "Pollution Research, Toxicity Studies", 64th Annual Report, State of Wash. Dept. of Fish. (1954).
- (g) Fujiya, M., "Use of Electrophoretic Serum Separation in Fish Studies", Jour. Water Pollution Control Fed. (1961).
- (v) Aluminum Chloride AlCl_3 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

Toxicity:

When aluminum chloride was dissolved in tap water at pH 7.2-7.4, concentrations of aluminum in excess of 0.5 mg/litre were fatal to various fishes. Young eels died within 3.6 hours in a solution of aluminum chloride containing 2.7 mg/litre of aluminum but they tolerated 0.27 mg/litre for 50 hours (a). Wallen et al. (aa) studied the effect of aluminum chloride on the mosquito-fish (*Gambusia affinis*) in highly turbid water at 20-21°C. They found a 96-hour TL_m value of 133 mg/litre. This dosage reduced the turbidity from 230 mg/litre to less than 25 mg/litre.

The following concentrations of aluminum chloride have been reported to be lethal to various test fish in sea water:

<u>Concentration of AlCl₃ in mg/ litre</u>	<u>Type of Water</u>	<u>Test Organism</u>	<u>Effect</u>	<u>Reference</u>
88	Sea water	Redfish	Killed quickly	b
88	Sea water	Other fish	Killed more slowly	c
132	Sea water	All fish tested	Most killed in a few hours, all in a few days	d
176	Sea water	All fish tested	All killed in a few hours	e

The foregoing information shows a wide variation in the toxic level of AlCl₃ toward fish. In a similar manner, there is no consistent pattern of toxicity toward lower forms of aquatic life. Using water from the River Havel from which the test organisms were recovered, Bringmann and Kuhn (f) studied the threshold effects of aluminum chloride on various organisms during an exposure of 4 days at 23-27°C. They found that Daphnia withstood a concentration of 1000 mg/litre as aluminum whereas Scenedesmus exhibited toxic effects at 1.5-2.0 mg/litre of aluminum. In contrast, the threshold concentration of aluminum chloride (AlCl₃) for immobilization of Daphnia magna in Lake Erie waters at 25°C was found to be less than 6.7 mg/litre, for a 64-hour period (g).

Oysters do not appear to be sensitive to the action of AlCl₃ in seawater (h).

- (a) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts", Sewage and Industrial Wastes (1953).
- (aa) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (b) Pulley, T.E., "Effect of Aluminum Chloride in Small Concentrations on Various Marine Organisms", Texas Jour. Sci. (1950).
- (c) See (b) above.
- (d) See (b) above.
- (e) See (b) above.
- (f) Bringmann, G., and Kuhn, R., "The Toxic Effects of Waste Water on Aquatic Bacteria, Algae, and Small Crustaceans", Gesundheits-Ing. (1959).
- (g) Anderson, B.G., "The Apparent Thresholds of Toxicity of *Daphnia magna* for Chlorides of Various Metals When Added to Lake Erie Water", Trans. Am. Fish. Soc. (1948); Water Pollution Abs. (1950).
- (h) Meinck, F., Stooff, H., and Kohlschutter, H., "Industrial Waste Waters (Industrie-Abwasser)", 2nd Edition, Gustav Fischer Verlag. Stuttgart (1956).

(C) Depressing Agents

Depressing agents assist in the separation of one mineral from another when the floatabilities of the two minerals to be separated are quite similar for any given collector or collector combination. Before the development

of specific depressants, it was difficult, if not impossible, to separate by froth flotation minerals which had the same or quite similar floatabilities with any collector-frother combination. Depressants were developed, therefore, to force specific minerals (which would normally float under a given set of conditions) to remain in the ore pulp while other minerals were being floated.

Toxicity of Specific Depressing Agents

(i) Sodium Cyanide (NaCN)

Uses: Alkaline cyanides are strong depressants of the iron sulphides (pyrite, pyrrhotite and marcasite), arsenopyrite and sphalerite. To a lesser extent, they act as depressants for chalcopyrite, enargite, tennantite, bornite and most other sulphide minerals.

Toxicity:

The following concentrations of sodium cyanide have been shown to be harmful or toxic to fish:

<u>Concentration of NaCN in mg/ litre</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Remarks</u>	<u>Reference</u>
0.05	124 hours	Trout	100 percent mortality	a
0.28	96 hours	Bluegills	TL _m in soft water	b
0.33-0.35	2.5 hours	Minnows	Lethal	c
0.4	1 hour	Minnows	Stopped eating	d
0.43	96 hours	Fathead minnows	TL _m in soft water	e
0.44	48 hours	Fathead minnows	TL _m	f
0.5	4 to 6 hours	Goldfish and green sun- fish	Lethal, 25°C	g
0.5-0.7	24 hours	Minnows	25 percent mortality	h
0.66	96 hours	Fathead minnows	TL _m in hard water	i
0.75	24 hours	Minnows	50 percent mortality	j
0.8	24 hours	Minnows	100 percent mortality	k
1.0	0.7 to 10 hours	Mixed fish	Lethal at 25°C	l
1	20 min- utes	Trout	100 percent mortality	m
1.5	0.6 to 24 hours	Goldfish and green sun- fish	Lethal	n
2	47 min- utes	Trout	Lethal	o
2.0	--	Sticklebacks	Lethal at 17°C	p
3.1	90 min- utes	Fish	Depressed respiration	q
4.3		Hardy carp	Paralyzed	r
5	12 min- utes	Shiner	Killed	s
5	2 hours	Trout, Blue- gills	Killed	t
10	4 min- utes	Shiner	Killed	u

- (a) Dobson, J.G., "Disposal of Cyanide Wastes", Metal Finishing (1947).
- (b) Henderson, C., Pickering, Q.H., and Lencke, A.E., "The Effect of Some Organic Cyanides (Nitrites) on Fish", Proc. 15th Industrial Waste Conf. (1960), Engineering Bull. Purdue Univ. (1961).
- (c) Blabaum, C.J., and Nichols, M.S., "Effects of Highly Chlorinated Drinking Water on White Mice", Jour. A.W.W.A. (1956).
- (d) Schaut, G.G., "Fish Catastrophes During Drought", Jour. A.W.W.A. (1939).
- (e) See (b) above.
- (f) Black, H.H., McDermott, G.N., Henderson, C., Moore, W.A., and Pahren, H.R., "Industrial Waste Guide, By-Product Coke", Proc. 11th Industrial Waste Conf., Purdue University (1957).
- (g) Bridges, W.P., "Sodium Cyanide as a Fish Poison", Special Scientific Report Fisheries No. 253, U.S. Dept. Interior (1958).
- (h) See (d) above.
- (i) See (e) above.
- (j) See (d) above.
- (k) See (d) above.
- (l) See (g) above.
- (m) See (a) above.
- (n) See (g) above.
- (o) Smith, R.T., "Cyanide Bearing Ore Mill Refuse as a Menace to Fish Life", Science (1938).

- (p) Jones, J.R.E., "Fish and River Pollution", Chapter 7 of "Aspects of River Pollution", L. Klein, Editor, Butterworth Scientific Publ., London (1957).
- (q) Jones, J.R.E., "The Oxygen Consumption of *Gasterosteus Aculeatus* L. in Toxic Solutions", Jour. Exp. Biol. (1947); Water Pollution Abs. (1947).
- (r) See (d) above.
- (s) See (a) above.
- (t) Applegate, V.C., Howell, J.H., Hall, A.E., and Smith, M.A., "Toxicity of 4,346 Chemicals to Larval Lampreys and Fishes", Fish and Wildlife Service, Special Sci. Rept. Fish. (1957).
- (u) See (a) above.
- (ii) Lime (CaO or $\text{Ca}(\text{OH})_2$)

Uses: For depressing pyrite and other iron sulphides.

For depressing cobalt sulphides.

Toxicity:

See section concerning 'bulk chemicals'.

- (iii) Sodium and Calcium Sulphites and Hyposulphites and Sodium Hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$)

Uses: Depressing pyrite and sphalerite in the flotation of copper minerals.

Toxicity:

The lethal concentration of sodium sulphite to goldfish in 96 hours at $18-23^\circ\text{C}$ has been reported (a) as

100 mg/litre; but on the other hand, concentrations up to 260 mg/litre at pH 5 to 9 have been observed to be harmless to young carp (b). Using turbid water at 18-26°C, Wallen et al. (c) found the 24-, 48-, and 96-hour TL_m for mosquito-fish to be 2600 mg/litre.

The toxic threshold concentration of sodium sulphite for the flatworm, *Polycelis nigra*, was found to be 7580 mg/litre (d). The minimum lethal concentration for *Daphnia* has been reported to be 300 mg/litre (e, f). For the immobilization of *Daphnia magna* in Lake Erie water at 25°C, the threshold concentration of sodium sulphite has been reported to be 440 mg/litre (g) and 3784 mg/litre (h).

- (a) Jones, J.R.E., "Fish and River Pollution", Chapter 7 of "Aspects of River Pollution", L. Klein, Editor, Butterworth Scientific Publ., London (1957).
- (b) Tomiyama, T., and Yamagawa, A., "The Effect of pH Upon Toxic Effects of Sulphide and of Sulphite on Young Carp", Bull. Jap. Soc. Sci. Fish. (1950); Water Pollution Abs. (1953).
- (c) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (d) Jones, J.R.E., "A Study in the Relative Toxicity of Anions, With *Polycelis nigra* (Planarian) as Test Animal", Jour. Exp. Biol. (1941).

- (e) Rudolfs, W., Barnes, G.E., "Review of Literature on Toxic Materials Affecting Sewage Treatment Processes, Streams, and B.O.D. Determinations", Sewage and Industrial Wastes (1950).
- (f) Anon., "The Toxicity of Kraft Pulping Wastes to Typical Fish Food Organisms", Tech. Bull. National Council for Stream Improvement (1947).
- (g) Anderson, B.G., "The Toxicity Thresholds of Various Sodium Salts Determined by the Use of *Daphnia magna*", Sewage Works Jour. (1946).
- (h) Anderson, B.G., "The Toxicity Thresholds of Various Substances Found in Industrial Wastes as Determined by the Use of *Daphnia magna*", Sewage Works Jour. (1944).

(iv) Zinc Sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$

Uses: In conjunction with cyanide, or alone, for the depression of sphalerite while floating lead and copper minerals.

Toxicity:

The following concentrations of zinc sulphate, as the salt or as zinc, have been reported lethal to fish in the stated time of exposure:

<u>Concentration of Zinc Sul- phate, mg/ litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Fish</u>	<u>Reference</u>
0.13 (as Zn)	--	--	Guppy	a
0.3 (as Zn)	--	Long term	Sticklebacks	b
0.4 (as Zn)	--	7 days	Sticklebacks	c
0.7 (as Zn)	--	4 days	Sticklebacks	d
0.8	--	144 minutes	Minnows	e
1.5	Soft	24 hours	Sticklebacks	f
3-6 (as Zn)	Tap	48 hours	Young trout	g
4.0	--	144 minutes	Minnows	h
6.0 (as Zn)	Tap	14 hours	Trout fingerlings	i
8.1	--	72 minutes	Minnows	j
10	Fresh	--	Fish	k
10	--	20 hours	Trout	l
10	Fresh	48 hours	Minnows	m
16*	--	20 hours	Young eels	n
25	Distilled	133 minutes	Rainbow trout	o
25-50 (as Zn)	Tap	2 hours	Rainbow trout	p
100	--	5 days	Goldfish	q, r
400	Distilled	200 minutes	Minnows	s
1000	Hard	1-4 hours	Goldfish	t

* Approximately

- (a) Shaw, W.H.R., and Lawrence, B.R., "Bioassay for the Estimation of Metal Ions", Anal. Chem. (1956).
- (b) Murdock, H.R., "Industrial Wastes. Some Data on Toxicity of Metals in Wastes to Fish Life are Presented", Ind. Eng. Chem. (1953).
- (c) See (b) above.
- (d) See (b) above.
- (e) Carpenter, K.E., "The Lethal Action of Soluble Metallic Salts on Fishes", Brit. Jour. Exp. Biol. (1927).

- (f) Meinck, F., Stoaff, H., and Kohlschutter, H., "Industrial Waste Waters (Industrie-Abwasser)", 2nd Edit. Gustav Fischer Verlag, Stuttgart (1956).
- (g) Goodman, J.R., "Toxicity of Zinc for Rainbow Trout (*Salmo gairdnerii*)", Cal. Fish and Game (1951).
- (h) See (e) above.
- (i) See (g) above.
- (j) See (e) above.
- (k) Ellis, M.M., "Pollution of the Coeur d'Alene River and Adjacent Waters by Mine Wastes", U.S. Bur. Fish. Spec. Sci. Rept. (1940).
- (l) See (f) above.
- (m) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts", Sewage and Industrial Wastes (1953).
- (n) See (m) above.
- (o) Grindley, J., "Toxicity to Rainbow Trout and Minnows of Some Substances Known to be Present in Waste Waters Discharged to Rivers", Ann. Appl. Biol. (1946); Water Pollution Abs. (1946).
- (p) See (g) above.
- (q) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (r) Anderson, B.G., "The Apparent Thresholds of Toxicity of *Daphnia magna* for Chlorides of Various Metals When Added to Lake Erie Water", Trans. Amer. Fish. Soc. (1948); Water Pollution Abs. (1950).

(s) See (α) above.

(t) See (α) above.

Typical Commercial Specification for Zinc Sulphate
Monohydrate:

Appearance:	Free-flowing powder or granules
Zinc Sulphate Monohydrate:	98% min.
Zinc Equivalent:	36% min.
Iron:	0.02% max.
Lead:	0.002% max.
Copper:	0.0012% max.
Cadmium:	0.005%
Arsenic:	0.0001% max.

Grade Available

Granular:	Mesh size -6 + 14
Regular:	Mesh size -16 + 52
Powder:	Mesh size -200

(v) Sodium Silicate (Na_2SiO_3)

Uses: Used for the depression of quartz and other
silicate minerals.

Toxicity:

The 100-hour toxicity threshold of sodium silicate

in double-distilled water at 23°C to *Daphnia magna* has been reported (a) at 247 mg/litre with a resulting pH value of 9.1, but in the presence of other sodium salts this threshold may be somewhat lower.

The Water Pollution Research Board of England determined that sodium silicate was not lethal to fingerling rainbow trout at a concentration of 256 mg/litre. Using turbid water at 21-22°C, Wallen et al. (b) found that the 96-hour TL_m for the mosquito-fish (*Gambusia affinis*) was 2320 mg/litre.

(a) Freeman, L., and Fowler, I., "Toxicity of Combinations of Certain Inorganic Compounds to *Daphnia magna* (Straus)", Sewage and Industrial Wastes (1953).

(b) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).

(vi) Sodium Hydroxide (NaOH)

Uses: For depression of stibnite

Toxicity:

See section concerning 'bulk chemicals'

(vii) Sulphuric Acid (H_2SO_4)

Uses: For quartz depression. Absorption of metal ions is prevented on quartz by suppression of ionization of the silicic acids on the quartz surface.

Toxicity:

See section concerning 'bulk chemicals'

(viii) Hydrofluoric Acid (HF)

Uses: For depressing quartz in the flotation of feldspar with cationic collectors.

Toxicity:

Hydrogen fluoride, a colourless gas, is very soluble in water and dissociates into hydrogen and fluoride ions. Hydrogen fluoride, as an entity, is reported to be harmful to fish at 40 mg/litre and lethal at 60 mg/litre (a).

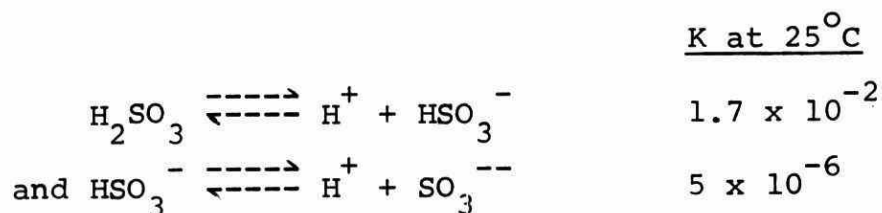
- (a) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee", Report No. 3 (1950).

(ix) Sulphur Dioxide (SO_2)

Uses: Usually in conjunction with causticized starch, to separate or depress galena while floating copper sulphides.

Toxicity:

A colourless, nonflammable gas with a suffocating odour, sulphur dioxide is soluble in water to the extent of over 100,000 mg/litre at 20°C. The dissolved gas combines with water to form sulphurous acid; thus, $\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$ and the sulphurous acid dissociates according to the equations:



The percentages of undissociated sulphurous acid, HSO_3^- , and sulphite ion at various pH values are shown by the following tabulation:

pH	H_2SO_3	Percent as HSO_3^-	SO_3^{--}
4	0.56	94.7	4.74
5	0.04	66.5	33.46
6	--	16.7	83.3
7	--	2.0	98.0
8	--	0.2	99.8
9	--	0.02	99.98

Very little of the sulphurous acid remains undissociated in the normal pH ranges; at pH 5 and below, HSO_3^- predominates and above 5 the bivalent sulphite ion prevails.

In the presence of oxidizing agents such as dissolved

oxygen and chlorine, the sulphite ion is gradually oxidized to sulphate, the sulphur changing from a + 4 valence to + 6.

In 1917, Shelford (a) reported that 16 to 19 mg/litre of sulphur dioxide killed orange-spotted sunfish in one hour. Ellis (b) quotes references to the effect that concentrations of SO_2 of 10 mg/litre in tap water caused trout to float helplessly within 10 minutes, and Ellis (c) also reported that 5.0 mg/litre of SO_2 kills trout in one hour. According to Bandt (d), 0.5 mg/litre of sulphurous acid is toxic to fish. Sulphurous acid is lethal to tench at a concentration of 1.0 mg/litre for two hours (e).

- (a) Shelford, V.E., "An Experimental Study of the Effects of Gas Waste Upon Fishes, With Especial Reference to Stream Pollution", Bull. Ill. State Lab. Nat. Hist. (1917).
- (b) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. 22 (1937).
- (c) Ellis, M.M., "Pollution of the Coeur d'Alene River and Adjacent Waters by Mine Wastes", U.S. Bur. Fish. Spec. Sci. Rept. (1940).
- (d) Bandt, H.J., "Waste Waters from Suction Gas Plants", Gesundh-Ing. (1940); Jour. A.W.W.A. (1946).
- (e) Meinck, F., Stoof, H., and Kohlschutter, H., "Industrial Waste Waters (Industrie-Abwasser)", 2nd Edit. Gustav Fischer Verlag. Stuttgart (1956).

(x) Quebracho and Tannic Acids ($C_{76}H_{52}O_{46}$)

Uses: For the depression of calcite and dolomite in fatty acid flotation of fluorite or scheelite as well as pyrite.

Toxicity (Tannic Acid):

The lethal doses reported for fish vary widely and depend on the species tested and the conditions of the experiment. At least 0.4 mg/litre is required to affect most fish and some species can survive 10 mg/litre or more, according to Westfall and Ellis (a); yet Ellis (b) reports that 10 mg/litre in hard water was not injurious in 100 hours to goldfish, but that 100 mg/litre killed in 9 to 20 hours. Belding (c) quotes references to the effect that the lethal doses to kill in 24 hours were 6.25 mg/litre for trout, 71 mg/litre for minnows and 142 mg/litre for goldfish. Schaut (d) found that minnows lost their appetite in 17.1 mg/litre of tannic acid but did not die.

Using highly turbid water and the mosquito-fish (*Gambusia affinis*) as the test organism, Wallen et al. (e) found the 24- and 48-hour TL_m for tannic acid to be 41 mg/litre while the 96-hour TL_m was 37 mg/litre. The addition

of tannic acid increased the turbidity from an initial 135 mg/litre to 170 mg/litre, but lowered the pH only from 7.3 to 6.7. The State of Washington Department of Fisheries (f) found the critical level for young chinook salmon to be 1.73 to 2.85 mg/litre for a 72-hour exposure in flowing fresh water and below 1.70 mg/litre in flowing sea water.

According to Doudoroff and Katz (g), tannic acid can be toxic to fish without lowering the pH to 5.0. Toxicity is then attributable chiefly to the undissociated acid in solution and hence pH is not a reliable index of dangerous pollution.

In Lake Erie water, according to Anderson (h) the threshold concentration for immobilization of *Daphnia magna* after prolonged exposure at 25°C was 26 mg/litre, but it may be as low as 3.0 mg/litre.

- (a) Westfall, B.A., and Ellis, M.M., "Pulp-Mill Pollution of the Rainy River Near International Falls, Minnesota", Dept. of Interior, Spec. Sci. Rept. (1944).
- (b) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. 22 (1937).
- (c) Belding, D.L., "Toxicity Experiments With Fish in Reference to Trade Waste Pollution", Trans. Amer. Fish. Soc. (1927).

- (d) Schaut, G.G., "Fish Catastrophes During Drought", Jour. A.W.W.A. (1939).
- (e) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (f) Anon., "Toxic Effects of Organic and Inorganic Pollutants on Young Salmon and Trout", State of Washington, Dept. Fisheries Res. Bull. (1960).
- (g) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Toxic Components to Fish", Sewage and Industrial Wastes (1950).
- (h) Anderson, B.G., "The Toxicity Thresholds of Various Substances Found in Industrial Wastes as Determined by the Use of *Daphnia magna*", Sewage Works Jour. (1944).

(xi) Ferrocyanide

Uses: For the depression of copper sulphides in molybdenite flotation and in the separation of certain copper sulphides from sphalerite.

Toxicity (Potassium Ferrocyanide - $K_4Fe(CN)_6$):

This compound, in which the iron is in the reduced or ferrous condition, is readily soluble in water but the complex ions decompose slowly to release cyanide ion.

Schaut (a) reports that minnows exposed for 70 days to 17.1 mg/litre of potassium ferrocyanide in stabilized tap water showed no harmful effects, and Ellis (b) quotes

references to show that 2000 mg/litre were not lethal to minnows and goldfish. Trout survived a one-hour exposure to 8,723 mg/litre in tap water without symptoms (c).

Burdick and Lipschuetz (d) noted that fish were killed in a New York stream by the discharge of an industrial waste containing ferro- and ferricyanides when the concentration of the diluted compounds was far less than the generally accepted lethal doses (as noted above). The authors reported that these compounds decompose under the action of sunlight, especially in the presence of dissolved oxygen, to release cyanogen, HCN, and cyanides. Part of the HCN is lost to the atmosphere. In diffuse light, 4000 mg/litre of potassium ferrocyanide in solution showed a cyanide content of 0.3 to 0.6 mg/litre and killed all fish in 48 hours. This toxic effect is not evident in solutions of 2000 mg/litre in diffuse light or in the dark. In direct sunlight, however, the following effects upon fish were noted:

<u>Concentration of Potassium Ferrocyanide in mg/litre</u>	<u>Resulting Concentration of Cyanide, mg/litre</u>	<u>Effects</u>
1	0.05 to 0.16	No harm in 5 hours
2	0.36 to 0.48	Fish died in 0.5 to 1.5 hrs.
3	0.72	Fish died in 25 minutes
5	0.50 to 0.84	Fish died in variable times

Using water of the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (e) found that the median threshold effect of potassium ferrocyanide occurred as follows:

<u>Test Organism</u>	<u>Temperature</u> °C	<u>Time of Exposure</u>	<u>Threshold Concentration in mg/litre as Fe(CN)₆</u>
Scenedesmus	24	4 days	0.2
Escherichia coli	27	1-2 days	over 1000

Toxicity (Sodium Ferrocyanide - $\text{Na}_4\text{Fe}(\text{CN})_6$):

This compound, containing reduced iron, is highly soluble in water. In aqueous solution, it decomposes under the action of sunlight to release cyanide ion and HCN.

For *Daphnia magna* in Lake Erie water at 25°C, the

toxic concentration was reported by Anderson (f) to be less than 600 mg/litre, or about 540 mg/litre (g). For *Polycelis nigra*, a planarium, Jones (h) found the toxic threshold to be 170 mg/litre. It should be recognized, however, that under the action of sunlight with the resultant decomposition to cyanides, this compound may be much more lethal.

- (a) Schaut, G.G., "Fish Catastrophes During Drought", Jour. A.W.W.A. (1939).
- (b) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. 22 (1937).
- (c) See (b) above.
- (d) Burdick, E.B., and Lipschuetz, M., "Toxicity of Ferro and Ferri Cyanide Solutions to Fish, and Determination of the Cause of Mortality", Trans. Am. Fish. Soc. (1948).
- (e) Bringmann, G., and Kuhn, R., "The Toxic Effects of Waste Water on Aquatic Bacteria, Algae, and Small Crustaceans", Gesundheits-Ing. (1959).
- (f) Anderson, B.G., "The Toxicity Thresholds of Various Sodium Salts Determined by the Use of *Daphnia magna*", Sewage Works Jour. (1946).
- (g) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee", Report No. 3 (1950).
- (h) Jones, J.R.E., "A Study in the Relative Toxicity of Anions, With *Polycelis nigra* (Planarian) as Test Animal", Jour. Exp. Biol. (1941).

(xii) Ferro and Ferricyanides

Uses: For separating cobalt and nickel sulphides from copper sulphides.

Toxicity (Potassium Ferricyanide - $K_3Fe(CN)_6$):

This compound differs from the ferrocyanide in that the iron is trivalent. Potassium ferricyanide is slowly but highly soluble in water, and an aqueous solution decomposes gradually, especially in sunlight.

According to Schaut (a), minnows exposed to 17.1 mg/litre of potassium ferricyanide for one hour in stabilized tap water showed no harm, and Ellis (b) quotes references to the effect that 2000 mg/litre of this compound had no lethal action on minnows and goldfish. It is important to recognize, however, that the ferricyanide and ferrocyanide ions decompose slowly with the release of cyanide ion and the formation of HCN, which is much more toxic than the complex ions. Burdick and Lipschuetz (c) recognized this phenomenon and demonstrated that concentrations of ferricyanide as low as 2.0 mg/litre in the presence of sunlight became toxic to fish life (d, e, f, g). In hot, bright summer weather, this limit might be even lower, according to the authors. A toxic

limit as low as 0.5 mg/litre of ferricyanide has been reported (h). Hiatt et al. (i) found that 1.0 mg/litre of potassium ferricyanide produced a slight irritant activity in marine fish.

Using water from the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (j) found the median threshold effect of potassium ferricyanide to occur as follows:

<u>Organism</u>	<u>Temperature</u> °C	<u>Time of</u> <u>Exposure</u>	<u>Threshold Concentration</u> in mg/litre as $\text{Fe}(\text{CN})_6$
Scenedesmus	24	4 days	0.25
Daphnia	23	2 days	2.5
E. coli	27	1-2 days	over 1000

- (a) Schaut, G.G., "Fish Catastrophes During Drought", Jour. A.W.W.A. (1939).
- (b) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. 22 (1937).
- (c) Burdick, E.B., and Lipschuetz, M., "Toxicity of Ferro- and Ferri-Cyanide Solutions to Fish, and Determination of the Cause of Mortality", Trans. Am. Fish. Soc. (1948).
- (d) Henderson, C., and Tarzwell, C.M., "Bio-Assays for Control of Industrial Effluents", Proc. 12th Industrial Waste Conf., Eng. Bull. Purdue Univ. (1958).

- (e) Black, H.Y., McDermott, G.N., Henderson, C., Moore, W.A., and Pahren, H.R., "Industrial Wastes Guide -- By-Product Coke Industry", Sewage and Industrial Wastes (1957).
- (f) Tarzwell, C.M., "Disposal of Toxic Wastes", Ind. Wastes (1958).
- (g) Neil, J.H., "Toxicity of Cyanides to Fish", Third Ontario Ind. Wastes Conf., Pollution Control Board of Ontario (1956).
- (h) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee", Report No. 3 (1950).
- (i) Hiatt, R.W., Naughton, J.J., and Mathews, D.C., "Relation of Chemical Structure to Irritant Responses in Marine Fish", Nature, Lond. (1953).
- (j) Bringmann, G., and Kuhn, R., "The Toxic Effects of Waste Water on Aquatic Bacteria, Algae, and Small Crustaceans", Gesundheits-Ing. (1959).

(xiii) Permanganate

Uses: For depression of pyrrhotite and pyrite in the presence of arsenopyrite. Also used in some instances in copper-molybdenite separations where the copper minerals are depressed with permanganate.

Toxicity (Potassium Permanganate - KMnO_4):

Potassium permanganate is a powerful oxidizing agent and it is sometimes used as a bactericide. It is frequently used to disinfect fish tanks and to treat certain

fish infections, such as fungus growths. In concentrations of 0.2 to 0.5 mg/litre, it has been effective as an algicide in reservoirs.

The threshold concentration of potassium permanganate for the immobilization of *Daphnia magna* has been reported to be 0.63 mg/litre (a). In river water, 5 mg/litre has killed various minute crustaceans, including fishfood organisms (b).

The following concentrations of potassium permanganate have been toxic or lethal to fish:

<u>Concentration in mg/ litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Type of Fish</u>	<u>Reference</u>
3.0	--	--	Bluegills	c
3.2	Tap	24 hour TL _m	Fingerling catfish	d
4.0	--	--	Largemouth bass	e
5.0	--	--	Fathead minnows	f
5.2		24-hour TL	Bluegill sunfish	g
5.4		48-hour TL _m	Bluegill sunfish	h
6.25	--	24 hours	Trout	i
10	Hard	12-18 hours	Goldfish	j, k
11.8	--	8 hours	Young eels	l
12	Turbid	24 & 96-hour TL	Mosquito-fish	m
22-62	--	30 ^m minutes	Fish	n

- (a) Anderson, B.G., "The Toxicity Thresholds of Various Substances Found in Industrial Wastes as Determined by the Use of *Daphnia magna*", Sewage Works Jour. (1944).

- (b) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. 22 (1937).
- (c) Ludemann, D., "The Toxicity of Manganese to Fish, Crabs and Animals Forming the Food of Fish", Schr Reihe Ver. Wassergyg., No. 7 (1953); Water Pollution Abs. (1955).
- (d) Clemens, H.P., and Sneed, K.E., "Lethal Doses of Several Commercial Chemicals for Fingerling Channel Catfish", Special Scientific Report Fisheries No. 316, U.S. Dept. Interior (1959).
- (e) See (c) above.
- (f) See (c) above.
- (g) Turnbull, H., DeMann, J.G., and Weston, R.F., "Toxicity of Various Refinery Materials to Fresh Water Fish", Symposium on Waste Disposal in the Petroleum Industry, Ind. Eng. Chem. (1954).
- (h) See (g) above.
- (i) Belding, D.L., "Toxicity Experiments With Fish in Reference to Trade Waste Pollution", Trans. Amer. Fish. Soc. (1927).
- (j) See (b) above.
- (k) Jones, J.R.E., "Fish and River Pollution", Chapter 7 of "Aspects of River Pollution", L. Klein, Editor, Butterworth Scientific Publ., London (1957).
- (l) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts", Sewage and Industrial Wastes (1953).
- (m) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).

- (n) Kubena, M., "The Resistance of Fresh-Water Fish Toward Potassium Permanganate", Thesis, Coll. of Vet. Med. Brno; Water Pollution Abs. (1949).

(xiv) Chromate

Uses: For the depression of galena in copper-lead separators.

Toxicity:

The toxicity of chromium salts towards aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but lower forms of aquatic life are extremely sensitive, as the following information reveals:

<u>Concentration of Chromium mg/litre</u>	<u>Compound Used</u>	<u>Type of Fish</u>	<u>Remarks</u>	<u>Reference</u>
5	--	Fish	Toxic	a
5.2	$K_2Cr_2O_7$	Brown trout	Toxic	b
7.1	$K_2Cr_2O_7$	Carp	Not harmed	c
9	CrO_4	Fish	Toxic limit	d
10	$Na_2Cr_2O_7$	--	Only slightly hazardous	e
10	--	Silver salmon	Fresh water, toxic	f
17.8	--	Silver salmon	Sea water, toxic	g

<u>Concentration of Chromium mg/litre</u>	<u>Compound Used</u>	<u>Type of Fish</u>	<u>Remarks</u>	<u>Reference</u>
20	$K_2Cr_2O_7$ and K_2CrO_4	Rainbow trout	Toxic at 18°C	h, i, j
35.3	$K_2Cr_2O_7$	Goldfish	Not harmed	k
45	$K_2Cr_2O_7$	Bluegills	Tolerated in hard water for 20 days	l
50	$K_2Cr_2O_7$	Trout	Killed within 33 hours	m
50	--	Bluegills	Toxic limit for 30-day exposure	n
52	$K_2Cr_2O_7$	Young eels	Tolerated for 50 hours	o
52	CrO_3	Goldfish	Toxic in 30 minutes	p
52	CrO_3	Goldfish	Survived 4 days	q
68	$K_2Cr_2O_7$	Bluegills	Tolerated in hard water	r
70	--	Bluegills	Toxic limit for one week's exposure	s
75	$K_2Cr_2O_7$	Bluegills	Died within 4 days	t
83	$K_2Cr_2O_7$	Bluegills	Tolerated for 10 days	u
100	K_2CrO_4	Trout	24-hour TL_m	v
100	$K_2Cr_2O_7$	Trout	Fatal after 6 hours	w
103	$K_2Cr_2O_7$	Bluegills	96-hour TL_m	x, y, z
104	CrO_3	Goldfish	Toxic in 6 to 84 hours	aa, ab

<u>Concentration of Chromium mg/litre</u>	<u>Compound Used</u>	<u>Type of Fish</u>	<u>Remarks</u>	<u>Reference</u>
110	$K_2Cr_2O_7$	Sunfish	96-hour TL_m	ac, ad
113	$K_2Cr_2O_7$	Sunfish	96-hour TL_m	ae
130	$K_2Cr_2O_7$	Young eels	Tolerated over 50 hours	af
135	$K_2Cr_2O_7$	Sunfish	96-hour TL_m (hard water)	ag
145	$Na_2Cr_2O_7$	Bluegills	24-hour TL_m	ah
148	$Na_2Cr_2O_7$	Bluegills	Toxic limit	ai
170	K_2CrO_4	Sunfish	96-hour TL_m	aj, ak
177	$K_2Cr_2O_7$	Goldfish	Toxic in 3 days	al
180-362		Several species	Toxic	am
196	--	Large-mouth bass	TL_m	an
213	$Na_2Cr_2O_7$	Bluegills	48-hour TL_m	ao
300	Na_2CrO_4	Bluegills	24-hour TL_m	ap
520	K_2CrO_4	Young eels	Killed in 5-12 hours	ar

In highly turbid water, Wallen et al. (ar) found the 96-hour TL_m values for several chromate and dichromate compounds toward the mosquito-fish (*Gambusia affinis*) to be as follows:

<u>Compound</u>	<u>Temperature Range</u>	<u>pH Range</u>	<u>96-hour TL_m in mg/litre</u>	
			<u>For Compound</u>	<u>As Chromium</u>
Ammonium chromate	19-23°C	7.5-7.8	240	82
Ammonium dichromate	18-20	5.7-7.4	136	56
Potassium chromate	17-21	7.6-8.1	400	104
Potassium dichromate	21-23	5.4-6.7	280	99
Sodium chromate	20-22	7.7-8.6	420	135
Sodium dichromate	24-27	6.0-7.9	264	92

<u>Concentration of Chromium mg/litre</u>	<u>Compound Used</u>	<u>Type of Organism</u>	<u>Remarks</u>	<u>Reference</u>
0.016	Na ₂ Cr ₂ O ₇	Daphnia magna	Toxic threshold	as
0.05	--	Daphnia magna	Killed in 6 days	at
<<0.10*	Na ₂ Cr ₂ O ₇	Daphnia magna	Toxic threshold	au
<<0.10*	Na ₂ CrO ₄	Daphnia magna	Toxic threshold	av
0.21	K ₂ Cr ₂ O ₇	Protozoan (Microregma)	Threshold effect	aw
0.21	K ₂ Cr ₂ O ₇	Diatom (Navicula)	Softwater TL _m , 22°C	ax
0.25	K ₂ Cr ₂ O ₇	Diatom (Navicula)	Hardwater TL _m , 22°C	ay
0.51	Na ₂ CrO ₄	Daphnia magna	Toxic threshold	az
0.7	K ₂ Cr ₂ O ₇	Daphnia	Threshold effect	ba
0.7	K ₂ Cr ₂ O ₇	Scenedesmus	Threshold effect	bb
0.7	K ₂ Cr ₂ O ₇	E. coli	Threshold effect	bc
1.4	Na ₂ CrO ₄	Gammarus pulex	Total mortality	bd
17.3	K ₂ Cr ₂ O ₇	Snail	Softwater TL _m , 20°C	be

<u>Concentration of Chromium mg/litre</u>	<u>Compound Used</u>	<u>Type of Organism</u>	<u>Remarks</u>	<u>Reference</u>
25.0	--	Midge fly larvae	Not toxic	bf
40.6	$K_2Cr_2O_7$	Snail	Hardwater TL _m , 20°C	bg
148	CrO_4	Polycelis nigra	Toxic threshold	bh

* signifies "very much less than"

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- (b) Southgate, B.A., "Treatment and Disposal of Industrial Waste Waters", Dept. of Scientific and Ind. Res., H.M. Stationery Office, London (1948).
- (c) Leon, A., "Carps vs. Sodium Chromate", Revista Technica IEM (Mexico) (1960); Pub. Health Engineering Abs. (1961).
- (d) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee", Report No. 3 (1950).
- (e) Martin, A.E., and Rostenbach, R.E., "Industrial Waste Treatment and Disposal" (At the Gov't Synthetic Rubber Plants, L.A. County, Cal.); Ind. and Eng. Chem. (1953).
- (f) Gooding, D., "Pollution Research, Toxicity Studies", 64th Annual Report, State of Wash. Dept. of Fish (1954).
- (g) See (f) above.
- (h) Grindley, J., "Toxicity to Rainbow Trout and Minnows of Some Substances Known to be Present in Waste Waters Discharged to Rivers", Ann. Appl. Biol. (1946); Water Pollution Abs. (1946).

- (i) Grindley, J., "Chromium Treatment", Jour. Soc. Chem. Ind. (1945); Chem. Abs. (1946).
- (j) Cairns, J., "The Effects of Increased Temperatures Upon Aquatic Organisms", Proc. 10th Ind. Waste Conf., Purdue Univ. Eng. Bull. (1956).
- (k) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (l) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts", Sewage and Industrial Wastes (1953).
- (m) See (l) above.
- (n) Klassen, C.W., Hasfurther, W.A., and Young, M.K., "The Toxicity of Hexavalent Chromium to Sunfish and Bluegills", Proc. 4th Ind. Waste Conf., Purdue Univ. (1948).
- (o) See (l) above.
- (p) See (k) above.
- (q) See (k) above.
- (r) See (l) above.
- (s) See (n) above.
- (t) See (l) above.
- (u) See (l) above.
- (v) Schiffman, R.H., and Fromin, P.O., "Chromium-Induced Changes in the Blood of Rainbow Trout, *Salmo gairdnerii*", Sewage and Industrial Wastes (1959).

- (w) See (l) above.
- (x) Cairns, J., Jr., and Scheier, A., "The Relationship of Bluegill Sunfish Body Size to Tolerance for Some Common Chemicals", Proc. 13th Industrial Waste Conf., Purdue Univ. Engineering Bull. (1959).
- (y) Cairns, J., Jr., and Scheier, A., "The Relationship of Bluegill Sunfish Body Size to Tolerance for Some Common Chemicals", Industrial Wastes (1958).
- (z) Anon., "The Relationship of Body Size of the Bluegill Sunfish to the Acute Toxicity of Some Common Chemicals", Philadelphia Academy of Sciences, Mimeo (1956).
- (aa) See (d) above.
- (ab) See (j) above.
- (ac) Trama, F.R., and Benoit, R.J., "Acute Toxicity of Hexavalent Chromium to the Common Eastern Sunfish", Presented at 134th Meeting of Amer. Chem. Soc., Chicago, Ill. (1958).
- (ad) Trama, F.B., and Benoit, R.J., "Toxicity of Hexavalent Chromium to Bluegills", Jour. of Water Pollution Control Federation (1960).
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- (af) See (l) above.
- (ag) See (ae) above.
- (ah) Abegg, R., "Some Effects of Inorganic Salts on the Blood Specific Gravity and Tissue Fluids of the Bluegill, *Lepomis macrochirus* Raf.", Physiol. Zool. (1950); Water Pollution Abs. (1950).
- (ai) See (d) above.

- (aj) See (ac) above.
- (ak) See (ad) above.
- (al) See (k) above.
- (am) See (l) above.
- (an) Fromm, P.O., and Shiffman, R.H., "Toxic Action of Hexavalent Chromium on Largemouth Bass", Jour. of Wildlife Management (1958); Biol. Abs. (1958).
- (ao) Turnbull, H., DeMann, J.G., and Weston, R.F., "Toxicity of Various Refinery Materials to Fresh Water Fish", Symposium on Waste Disposal in the Petroleum Industry, Ind. Eng. Chem. (1954).
- (ap) See (ah) above.
- (aα) See (l) above.
- (ar) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to Gambusia affinis of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (as) See (d) above.
- (at) Grushko, Y.M., "Toxic Substances and the Method of Establishing Hygienic Standards for Their Permissible Concentration in Water Reservoirs", Gigiena (1949); Chem. Abs. (1949).
- (au) Anderson, B.G., "The Toxicity Thresholds of Various Substances Found in Industrial Wastes as Determined by the Use of Daphnia magna", Sewage Works Jour. (1944).
- (av) See (au) above.
- (aw) Bringmann, G., and Kuhn, R., "Water Toxicology Studies with Protozoans as Test Organisms", Gesundheits-Ing. (1959).

(ax) See (ae) above.

(ay) See (ae) above.

(az) Fairchild, E.J., "Low Dissolved Oxygen. Effect Upon the Toxicity of Certain Inorganic Salts to the Aquatic Invertebrate *Daphnia magna*", Louisiana State Univ. Engineering-Experiment Station, Bull. (1955).

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(bc) See (ba) above.

(bd) Saurent, P., "Resistance of Fresh Water Crustaceans to the Action of Sodium Chromate", Verh. Int. Ver. Limnol. (1956) (1958); Water Pollution Abs. (1959).

(be) See (ae) above.

(bf) Surber, E.W., "Cricotopus bicinctus, a Midgefly Resistant to Electroplating Wastes", Trans. Amer. Fisheries Society (1959).

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(xv) Natural Colloids

This group of depressants includes organic colloids such as glue, gelatin, tannin, starch and quebracho extracts. These function as depressants in flotation by forming pro-

TECTIVE coatings on mineral surfaces thereby preventing collector coating and subsequent flotation. They are widely used as gangue controllers in copper, lead or zinc sulphide and precious metal flotation operations, as well as in non-metallic flotation operations.

(xvi) 'Commercial' Depressants

(a) Name: Aero Depressant 610

Company: Cyanamid

Toxicity:

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1,000 to 10,000 ppm ^w /v	relatively non-toxic

(b) Name: Aero Depressant 633

Company: Cyanamid

Toxicity:

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1,000 to 10,000 ppm ^w /v	relatively non-toxic

NOTE: A product called Aero Depressant 620 also appears in the above "600" series.

(c) Name: Tylose

Company: Hoechst

General (Tylose Brands):

Cellulose derivatives used as depressants for slime-forming minerals like kaolinite, talc, sericite, clay minerals, etc. Particularly successful brands are Tylose CR 50 in the flotation of sulphide minerals and Tylose CBR 4000 in the flotation of potassium salt; a large selection of other brands is marketed.

(D) Dispersants

In sulphide mineral flotation, the separation is ordinarily made in the presence of slimes, or very fine particles. However, for nonsulphide flotation where selectivity between species must be accomplished by subtle means, slime control is almost always necessary. In some cases (for example, the separation of clay from quartz), a dispersant can be added to the flotation system to ensure that coflocculation of the desired mineral and gangue does not occur. The term "slimes" is ambiguous and usually refers to a particle size below which the particles cannot be removed commercially. Fifty years ago, this was about 200 mesh (74 μ), but the widespread use of hydrocyclones has moved the usual definition down to 10 μ and finer.

Consider, for example, the mineral flocculation to be expected in a pulp of iron oxide (goethite), kaolinite, and finely ground quartz at pH 5. The goethite under these conditions is positively charged and would be expected to attract to its surface the very small particles of negatively charged kaolinite and quartz. These slime coatings seriously interfere with flotation. Even 50 mg/litre of bentonite clay slimes can completely inhibit the flotation of goethite. In addition to preventing collector attachment, slimes may also adsorb the collector, decreasing its availability to the mineral species to be floated. Amines are particularly sensitive to clay slimes.

Dispersion is usually accomplished through pH regulation and by dispersants, such as Calgon (hexametaphosphate), lignin sulfonates, sodium silicate, and tannin.

(E) Flocculants, Coagulants, Coagulant Aids, Etc.

A coagulant is a chemical which, in solution, furnishes ionic charges opposite to those of colloidal turbidity particles in the water. Coagulants neutralize repelling charges on colloidal particles of turbidity and produce jelly-like spongy masses called floc. Floc has an enormous surface

area per unit of volume that entraps or adsorbs particles of turbidity, organic matter, and bacteria.

Flocculation consists of mechanical entrapment of the agglomerated particles by adsorption onto the floc formed with coagulant chemicals and also by molecular bridging of the individual molecules of the coagulants. Although coagulation is a chemical reaction, the gathering in or adsorption of suspended solids is a mechanical process. Flocculation causes considerable increase in the size and density of coagulated particles, resulting in a faster rate of settling of the floc particles. The rate may be further accelerated through the use of a coagulant aid.

Coagulant aids are not, in themselves, coagulants but are of considerable assistance in the coagulation process. These chemicals form large floc particles that settle down through the solution and adsorb the particles of coagulated turbidity. Coagulant aids act as "binders" or "bridgers" in that they mechanically entrap or stick floc particles together. By creating larger and heavier flocs, coagulant aids speed up the settling process, facilitating better clarification at higher throughput rates.

Inorganic coagulants such as aluminum sulphate (alum), sodium aluminate, ferric and ferrous sulphate and various organic polyelectrolytes are commonly used to treat turbid waters.

Aluminum compounds, especially alum and sodium aluminate, are widely used coagulants. Both of these chemicals precipitate an aluminum hydroxide floc that has marked ability to remove suspended solids from water. The application of organic polyelectrolytes is, however, increasing where floc carryover is experienced and in waters extremely difficult to coagulate.

Generally, non-ionic organic polymers, bentonitic clays, and activated silica fall in the category of coagulant aids. Organic polyelectrolytes may be employed both as coagulant aids and coagulants, as they are ionically charged.

The term polymer refers to a general class of long chain molecules. Those polymers which are either cationic or anionic in nature are referred to as polyelectrolytes and those with no charge as non-ionic polymers.

Non-ionic polymers function as coagulant aids in a mechanical sense (as a binder) only. The non-ionic polymer

normally should be introduced at a point shortly after flocculation first occurs. It will "coat" the existing floc particles so that when they collide they will adhere to one another, thus forming larger floc particles.

In clarification of turbid waters, cationic polyelectrolytes function as primary coagulants. They are positively charged and will neutralize the negative surface charges on particles of turbidity, which then agglomerate. Anionic (negatively charged) polyelectrolytes function as co-coagulants, as they must be applied along with a cationic (positively charged) material which neutralizes the negative charge on turbidity. In softening applications, where precipitation particles are positively charged, however, anionic materials will coagulate alone.

Polyelectrolytes, because of their long chain molecule, also act as coagulant aids in that they will bind existing floc particles together into larger masses.

pH is a critically important factor when coagulation is based on inorganic coagulants, and the optimum pH varies with the inorganic coagulant employed. Often, the optimum pH for coagulation is not consistent with production of a

stable water, necessitating post-adjustment of pH with alkaline or acidic chemicals.

Coagulant aids are not markedly affected by pH and turbidity variation. Non-ionic organic polymers, poly-electrolytes and also bentonitic clays, will adsorb pinpoint floc and promote satisfactory floc growth even under conditions where pH and turbidity vary radically. They thus provide effective coagulation results over a much broader range of operations, simplifying control problems considerably.

Cold water slows chemical precipitation reactions. The standard rule is that chemical reaction rates are doubled for every 18°F. increase in temperature. For example, retention time for 32°F. water should be twice that for 50°F. water or four times that for 68°F. water. The newer organic polymers are, however, much less vulnerable to temperature influence than are the traditional inorganic coagulants.

Coagulating (etc.) agents are normally added after flotation to aid in the filtration of the products, or as an aid in thickening finely ground pulps. Lime, sulphuric acid, and natural and synthetic polymeric substances are the principal flocculation agents used (examples: guar,

starch, polyacrylamides).

Specific Common Flocculants, Coagulants, Coagulant Aids, Etc.,
Finding Use in the Mining Industry

(i) Name: Aerofloc 550 Reagent

Company: Cyanamid

Toxicity:

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	560 to 5,600 ppm ^w /v	relatively non-toxic

NOTE: Also in this series

Aerofloc 3425 Reagent

Aerofloc 3453 Reagent

(ii) Name: Superfloc 16 Flocculant

Company: Cyanamid

Chemistry: a polyacrylamide flocculant

Toxicity:

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	greater than 1,000 ppm ^w /v	relatively non-toxic

(iii) Name: Superfloc 20 Flocculant

Company: Cyanamid

Chemistry: a polyacrylamide flocculant

Toxicity:

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	greater than 1,000 ppm ^w /v	relatively non-toxic

(iv) Name: Superfloc 84 Flocculant

Company: Cyanamid

Chemistry: a polyacrylamide flocculant

Toxicity:

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	greater than 1,000 ppm ^w /v	relatively non-toxic

(v) Name: Superfloc 127 Flocculant

Company: Cyanamid

Chemistry: a polyacrylamide flocculant

Toxicity:

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	greater than 1,000 ppm ^w /v	relatively non-toxic

(vi) Other Common Commercial Flocculants, Etc., Used in the Mining Industry

(a) Dow Chemical Company

high molecular weight, water soluble, non-ionic, polyacrylamide-type products

Separan NP10
Separan NP20
Separan MGL

high molecular weight, water soluble,
anionic, polyacrylamide-type products

Separan AP30

aqueous solutions of the cationic polymer
polyethylenimine

PEI 1090
PEI 1130

(b) Hercules Powder Company

Hercofloc 824	nonionic
Hercofloc 817	low anionic
Hercofloc 833	medium anionic
Hercofloc 819	high anionic
Hercofloc 813	low cationic
Hercofloc 829	medium cationic
Hercofloc 832.1	very high cationic

Hercofloc polymers are synthetic, high molecular weight flocculants. Generally, these products are acrylamide-based copolymers.

(c) Float-Ore Limited (England)

(i) Liquid-Jelly "Flocobel" Flocculators

FC5, FC40, FC44, FC47

A series of anionic polymers and copolymers with

increasing anionic strength in higher numbers.

(ii) Powder Anionic Flocculators

FC18, FC19, FC160, FC170, FC180, FC187, FC190, FC200

A series of anionic polymers and copolymers of high molecular weight and increasing anionic strength in higher numbers.

(iii) Powder Superflocbels

FC109, FC119, FC170H, FC179, FC198

The range of anionic copolymers of extremely high molecular weight or with floc-reforming characteristics. These reagents are suitable particularly for high degree of compaction of settled solids.

(iv) Powder Cationic Flocculators

FC10, FC11

Polyacrylamide type copolymers with increased positive charge in FC11.

(v) Cationic Flocculators and Retention Aids

FC14, FC15, FC16, FC17

Polyacrylamide and Polyimines of various viscosities and strength.

(vi) Other Types of Flocculators

FC59, FC81

Polysaccharide types.

- (d) Nalco Chemical Company
Alchem Limited

Alchem D-173 Flocculant

A high molecular weight, water-soluble, non-ionic polymer flocculant.

Alchem D-176 Flocculant

A high molecular weight, water-soluble, anionic polymer flocculant.

Alchem D-178 Flocculant

A high molecular weight, water-soluble, non-ionic polymer flocculant.

Alchem D-179-M Flocculant

A high molecular weight, water-soluble anionic polymer flocculant.

Alchem 600

A slightly viscous liquid, high molecular weight, cationic polyelectrolyte, organic coagulant.

Specific gravity (60 ^o F)	1.070
--------------------------------------	-------

pH	9.0
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Alfloc 4151 Flocculant

A water-soluble polymer of very high activity and high molecular weight.

pH of 1.5% solution	8.2 ⁺ 0.5
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Alchem Hi-pHloc Liquid Flocculant

A stable, highly reactive, concentrated liquid flocculant containing sodium aluminate.

Nalcolyte 110A Potable Coagulant Aid

A water-soluble, non-ionic, high molecular weight polymer.

Nalco 2

A very stable, liquid sodium aluminate.

Nalco 600

A liquid, cationic polyelectrolyte.

Nalcolyte 603 Coagulation, Chemical and Filter Aid

A high activity, slightly viscous liquid organic polyelectrolyte.

Nalcolyte 610 Coagulation, Chemical and Filter Aid

A water-soluble, high activity, high molecular weight polymer.

Nalco 614

A free-flowing, granular type of sodium aluminate.

Nalco 650

A processed montmorillonite (clay).

Nalcolyte 672 Flocculant

A high molecular weight, anionic, water-soluble polymer.

Nalcolyte 673 Flocculant

An anionic, water-soluble polymer of high molecular weight.

Nalcolyte 675 Flocculant

A water-soluble polymer flocculant of high molecular weight.

Nalco 680

A pure-white sodium aluminate.

(e) Stein, Hall & Co., Inc.

Stein, Hall & Co., Inc., through its many subsidiaries throughout the world, manufactures over 700 types of reagents used in the mining industry. These reagents can be divided into two fields; depressants whose origin are carbohydrate based and flocculants which can be polysaccharide or polyacrylamide based. The basic trade names for the Stein, Hall products are JAGUAR and POLYHALL.

(i) JAGUAR

The Jaguar range of products is based on guar gum. The individual members of the Jaguar series have different characteristics which vary considerably. The flocculating properties of Jaguar are applied in three main categories:

- (a) Thickening
- (b) Filtration
- (c) Clarification

The guar gum molecule is essentially a straight chain mannan branched at quite regular intervals with single membered galactose units on alternate mannose units. Guar gum, chemically classified as a galactomannan, is a high molecular weight carbohydrate polymer or polysaccharide made up of many mannose and galactose units.

(ii) POLYHALL

Polyhall is a hydrocolloid of high molecular weight which is produced either as a complex synthetic non-ionic polyacrylamide or a hydrolyzed slightly anionic polyacrylamide.

Typical Stein, Hall Product Uses

Settling and Clarification

Jaguar MDD
Jaguar MD7A
Jaguar MRL22A
Polyhall M-19
Polyhall M-159
Polyhall M-295
Polyhall M-402

Filtration

Jaguar MDD
Polyhall M-295
Polyhall M-159
Polyhall M-402

Insol. Depression

Jaguar 703
Jaguar M-11/3
Jaguar MDB-2
Jaguar MDD
Jaguar 507
Reagent H-1
JCD73

Pyrrhotite Depression

Reagent F
JCD73

Selective Flocculation

Jaguar MDD
Jaguar 507
Polyhall M-402

Friction Loss

Polyhall M-295
Jaguar MDD

Other Stein, Hall Products

Polyhall 44-C
Polyhall 61
Polyhall M-630
Polyhall 35
Polyhall 250
Polyhall 39

MRL 332 (Anionic Backfill Flocculant)
MRL 91
MRL 201

Jaguar 387
Hallmark H-31
Stractan (Arabinogalactan)

(vii) Inorganic Coagulants, Etc.

(a) Aluminum Sulphate (Alum)

Formula: $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

Toxicity:

In fresh water, 7 mg/litre of aluminum sulphate has been reported to be fatal to *Fundulus* within 5 days and 14 mg/litre within 36 hours (a). Schaut (b) reported that 17.1 mg/litre of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was harmless to minnows in stabilized tap water during one hour of exposure. Sanborn (c) found that 100 mg/litre of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ did not affect goldfish, sunfish, and bass during seven days of exposure but that 250 mg/litre killed them in 8 to 24 hours. Wallen et al. (d) studied the effect of aluminum sulphate on the mosquito-fish (*Gambusia affinis*) in turbid water at 19-22°C. They found the 96-hour TL_m to be 235 mg/litre, at which concentration the turbidity was reduced from 180 mg/litre to less than 25 mg/litre, owing to the coagulating action of the alum.

The threshold concentration of aluminum sulphate for immobilization of *Daphnia magna* in Lake Erie water was found to be 106 mg/litre (e).

- (a) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts", Sewage and Industrial Wastes (1953).
- (b) Schaut, G.G., "Fish Catastrophes During Drought", Jour. A.W.W.A. (1939).
- (c) Keller, E.L., Simmonds, F.A., and Baird, P.K., "Some Observations on the Effect of Alum on Certain Sheet Properties of Paper", Paper Trade Jour. (1941); Water Pollution Abs. (1941).
- (d) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (e) Anderson, B.G., "The Toxicity Thresholds of Various Substances Found in Industrial Wastes as Determined by the Use of *Daphnia magna*", Sewage Works Jour. (1944).

(b) Ferric Sulphate

Formula: $\text{Fe}_2(\text{SO}_4)_3$

Toxicity:

Ellis (a) quotes a reference to the effect that a concentration of 0.716 mg/litre in distilled water killed shiners, carp, and suckers in 12 to 24 hours. In a solution of ferric sulphate in distilled water, a concentration of only 0.1 mg/litre of iron was reported to have killed certain fish within 24 hours (b).

In highly turbid water at 19-23°C, Wallen et

al. (c) found the 24-, 48-, and 96-hour TL_m concentrations for the mosquito-fish *Gambusia affinis*, to be 133 mg/litre. In Lake Huron water at 12°C, a concentration of 5.0 mg/litre of iron sulphate (valence not given) had no effect on rainbow trout, bluegill sunfish, or sea lamprey during a 24-hour period (d).

- (a) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. (1937).
- (b) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts", Sewage and Industrial Wastes (1953).
- (c) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (d) Applegate, V.C., Howell, J.H., Hall, A.E., and Smith, M.A., "Toxicity of 4,346 Chemicals to Larval Lampreys and Fishes", Fish and Wildlife Serv., Special Sci. Rept. Fish. (1957).

(c) Ferric Chloride

Formula: $FeCl_3$ and $FeCl_3 \cdot 6H_2O$

Toxicity:

The following concentrations of ferric chloride have been reported to be harmful or lethal to fish:

<u>Concentration of FeCl₃ in mg/ litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Species of Fish</u>	<u>Reference</u>
0.6	Tap	--	Goldfish	a
1.2	Tap	6 days	Stickleback	b
4.35	Tap	3 days	Goldfish	c
9	Distilled	20 hours	Goldfish	d
20	Tap	6 hours	Goldfish	e
74	Turbid	96-hour TL _m	Mosquito- fish	f
100	Soft	1.5 hours	Goldfish	g, h
540	--	86 minutes	Minnows	i
2700	--	69 minutes	Minnows	j
5400	--	54 minutes	Minnows	k

The following concentrations of ferric chloride were reported to be not harmful to fish:

<u>Concentration in mg/litre</u>	<u>Type of Water</u>	<u>Time of Exposure</u>	<u>Species of Fish</u>	<u>Reference</u>
1	Tap	10 days	Stickleback	l
5	--	50 hours	Young eels	m
10	Soft	96 hours	Goldfish	n
100	Hard	96 hours	Goldfish	o, p
270	--	90 minutes	Minnows	σ

- (a) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts", Sewage and Industrial Wastes (1953).

- (b) Anderson, B.G., "The Apparent Thresholds of Toxicity of *Daphnia magna* for Chlorides of Various Metals When Added to Lake Erie Water", Trans. Amer. Fish. Soc. (1948); Water Pollution Abs. (1950).
- (c) See (a) above.
- (d) Ellis, M.M., "Detection and Measurement of Stream Pollution (Related Principally to Fish Life)", U.S. Dept. of Commerce, Bur. of Fisheries Bull. 22 (1937).
- (e) See (a) above.
- (f) Wallen, I.E., Greer, W.C., and Lasater, R., "Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters", Sewage and Industrial Wastes (1957).
- (g) See (b) above.
- (h) See (d) above.
- (i) Carpenter, K.E., "The Lethal Action of Soluble Metallic Salts on Fishes", Brit. Jour. Exp. Biol. (1927).
- (j) See (i) above.
- (k) See (i) above.
- (l) See (b) above.
- (m) See (a) above.
- (n) See (d) above.
- (o) See (d) above.
- (p) See (b) above.
- (α) Anon., "Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee", Report No. 3 (1950).

Usage of Sulphide Flotation Chemicals in Actual Milling Circuits

In the sulphide flotation circuits of the Province of Ontario, the number of milling reagents employed and the daily consumption of each varies from property to property. Reagent use is a function of ore characteristics.

The following actual examples of reagent consumption in the Province of Ontario should serve to illustrate the reagent demand created by various sulphide ores.

Example #1

Ore Characteristics

In the general vicinity of the orebody, the rock consists of basic, intermediate and acid extrusives, ultrabasic and basic to intermediate intrusives and sedimentary rocks (all Precambrian in age). Within the extrusive and sedimentary rocks, graphitic zones are evident. Sericitization, chloritization, silicification, carbonatization, epidotization and serpentization are present in the above-mentioned rocks and are most predominant in and near the ore zone. The ore body contains sphalerite, chalcopyrite and pyrite with zones of massive pyritic ore containing varying amounts of sphalerite, galena and native silver.

pyrite 35% pyrrhotite less than 1%

sphalerite 20%

chalcopyrite 6%

galena 1.5%

native silver 10 oz./ton

chert 20%

sericite 10%

chlorite 2%

carbonate 2%

graphite 2%

Milling rate: 10,000 tons/day

Reagent Use:

<u>Reagent</u>	<u>Usage (lbs./ton ore milled)</u>
lime	2.85
soda ash	1.4
sulphur dioxide	0.9
Aerofloat 208 Promoter	0.16
Z-14	0.08
Aero Xanthate 317	0.09
M.I.B.C.	0.05
sodium cyanide	0.016
zinc sulphate	0.006
copper sulphate	1.75
Dowfroth 250	0.05

Example #2

Ore Characteristics

In the general vicinity of the orebody, the rock is composed of quartz feldspar biotite gneiss, iron formation, quartz feldspar pegmatite and some hornblende rich material. In some locations, quartz sericite biotite schist makes an appearance. The ore zone contains massive to disseminated

chalcopyrite, sphalerite, pyrrhotite, pyrite, quartz and minor galena.

chalcopyrite 4%

sphalerite 6%

galena 0.5%

pyrite 10%

pyrrhotite 12%

quartz 40%

magnetite 5%

Milling Rate: 1,700 tons/day

Reagent Use:

<u>Reagent</u>	<u>Usage (lbs./ton ore milled)</u>
lime	2.531
pine oil	0.013
copper sulphate	1.403
sodium cyanide	0.121
Z-6	0.039
Z-200	0.026
Sodium Aerofloat Promoter	0.070
Sodium sulphite	0.070
Dowfroth 250	0.006

Example #3

Ore Characteristics

The orebody in this case contains pyrite (42.5%), chalcopyrite (2.0%), sphalerite (16.0%), galena (1.5%), silica (23.0%), magnetite (3.0%) and miscellaneous gangue (12.0%).

Milling Rate: 2,500 tons/day

Reagent Use:

<u>Reagent</u>	<u>Usage (lbs./ton ore milled)</u>
soda ash	3.0
lime	3.0
sodium sulphite	1.2
copper sulphate	0.9
sulphur dioxide	0.22
M.I.B.C.	0.10
guar gum	0.075
Aerofloat 208 Promoter	0.07
Aerofloat 242 Promoter	0.035
Aero Xanthate 350	0.013
Aero Promoter 3501	0.002
sodium cyanide	0.06
Separan	0.005

Example #4

Ore Characteristics

The rock in the vicinity of the orebody is composed of peridotite, gabbro, volcanics (rhyolite), and minor iron formation. Minerals occurring within the orebody include pentlandite (7.6%), chalcopyrite (0.35%), pyrrhotite (13.0%), pyrite (5.0%), arsenopyrite (0.3%), talc, serpentine and carbonates.

Milling Rate: 700 tons/day

Reagent Use:

<u>Reagent</u>	<u>Usage (lbs./ton ore milled)</u>
amyl xanthate (collector)	0.30
copper sulphate (activator)	0.60
pine oil (frother)	0.60
tetrasodium pyrophosphate (slime dispersant)	0.20
Guartec (talc depressant)	0.95

Example #5

Ore Characteristics

The rock in the vicinity of the orebody is composed of quartz feldspar porphyry and acid volcanics. The acid

volcanic rocks consist dominantly of rhyolite and dacite flows with subordinate acid pyroclastic zones. Minor development of argillaceous sediments has been noted. The orebody itself is composed of massive pyrite lenses rich in chalcopyrite, sphalerite and argentiferous galena.

pyrite 35% pyrrhotite less than .5%

chalcopyrite 7%

sphalerite 22%

galena 1%

cassiterite (tin oxide) 0.5%

Milling Rate: 500 tons/day

Reagent Use: (a) copper circuit (b) zinc circuit

<u>Reagent</u>	<u>Usage (lbs./ton ore milled)</u>
lime (a)	4.0 to 4.5
zinc sulphate (a)	1.0 to 1.3
sodium isopropyl xanthate (a)	0.15 to 0.20
Dowfroth 250 (a)	0.05
lime (b)	2.5 to 3.5
copper sulphate (b)	1.0 to 1.5
sodium isopropyl xanthate (b)	0.15
Dowfroth 250 (b)	0.05

Metal Losses in Mine-Mill Circuits

Generally, ore is ground in ball or rod mills. During operation, a ball mill is kept about half full of steel balls (varying in size from three-quarters of an inch to approximately five inches) which, as the mill revolves, cascade and roll over each other. It is this action that grinds the ore. A rod mill differs from a ball mill in that steel rods instead of steel balls are used as the grinding media. The rods are two to four inches in diameter and are approximately the length of the interior of the mill itself.

The conditions, during operation, within the mills are extreme. As such, the rods and balls and even the mill liners wear out and have to be replaced. The metal loss from rods and balls (and from metallic liners if they are used) depends on the ore characteristics and, as such, varies from operation to operation.

NOTE: Autogenous grinding units are becoming quite common. These units force the ore to grind itself. Rods and balls are eliminated.

Since rods and balls, etc., are consumed during the milling process and since the metal is lost to waste, in a vague sense rods and balls, etc., can be con-

sidered to be mill "reagents". Some examples of typical metal losses in various mill circuits are given below:

Example #1

Geology

Ore minerals

Pentlandite 7.6%

Chalcopyrite 0.35%

Gangue minerals

Pyrrhotite 13.0%

Pyrite 5.0%

Arsenopyrite 0.3%

Talc

Serpentine

Carbonates

Country rock in the vicinity of the orebody

Peridotite

Gabbro

Volcanics (rhyolite)

Minor iron formation

Milling Rate: 700 tons/day

Mill Grind: 71% - 325 mesh

89% - 200 mesh

Total rod and/or ball metal losses: 5.0 lbs./ton ore

Example #2

Geology

The uranium bearing minerals are contained in a quartz pebble conglomerate. The ore contains approximately 8% pyrite.

Milling Rate: 3,400 tons/day

Mill Grind: 60% - 200 mesh

Total rod and/or ball metal losses: 1.2 lbs./ton ore

Example #3

Geology

The orebody consists of a compact grouping of massive pyrite lenses rich in copper, zinc and silver lying in an extensive development of diverse acid volcanic rocks.

Milling Rate: 500 tons/day

Mill Grind: 90 to 95% - 200 mesh

Total rod and/or ball metal losses: 3 lbs./ton ore

Example #4

Geology

The orebody consists of massive zones of chalcopyrite,

sphalerite, galena, native silver and pyrite. Siliceous material is found in the orebody. The country rocks consist of basic, intermediate, and acid extrusives, ultrabasic and basic to intermediate intrusives and (Precambrian) sedimentary rocks.

Milling Rate: 10,000 tons/day

Mill Grind: 95% - 325 mesh

Total rod and/or ball metal losses: 3.8 lbs./ton ore

Example #5

Geology

The orebody consists of several zones which, in general, contain massive and disseminated chalcopyrite, sphalerite, pyrrhotite, pyrite, quartz and minor galena. The country rock is feldspar biotite gneiss, quartz feldspar gneiss, and iron formation.

Milling Rate: 1,300 tons/day

Mill Grind: 54% - 200 mesh

Total rod and/or ball metal losses: 1.7 lbs./ton ore

MINE-MILL REAGENTS AND WASTEWATER RECYCLE

In the mining industry, wastewater recycle:

- (a) significantly reduces the volume of fresh water that is required daily to sustain processing operations;
- (b) significantly reduces the total volume of wastewater that is discharged to the environment;
- (c) reduces waste loadings from a property since reagent additions in the mill will, in all probability, be reduced. Also, precipitation, coagulation and settling effects in the tailings area, on a recycle basis, will tend to reduce overall waste loadings; and
- (d) reduces the required size of all waste treatment units due to the lower volume of all waste flows. Also, recycle permits the installation, if necessary, of very efficient and specific waste treatment units that are generally not available in sizes that are able to handle very large volume waste flows.

Total wastewater recirculation in the mining industry is not easy to attain. However, partial recycle is possible in nearly every case.

Wastewater recycle is most often complicated by the presence of residual quantities of certain persistent reagents

in the recycle stream. As a result, one or more circuits in the mill may not accept the recycle water. On the other hand, the presence of a specific residual reagent in a recycle stream could act to enhance certain operations and, in fact, could result in reduced overall reagent use in the mill.

At any rate, where residual reagents in a recycle stream are a problem, the following facts should be noted:

(1) Clean-up time in the reagent storage and mixing area of the mill can create problems. If the area is washed down after significant quantities of a particular reagent have been accidentally spilled, etc., or if cleaning of the area has been delayed, for various reasons, for several shifts, problems with the recycle water can result. Any 'slug' of reagent-rich waste from a reagent storage and mixing area that is discharged to a tailings area has the potential ability to influence the water quality of the recycle stream. Hours after the discharge, a minor or major mill upset could occur.

In essence, such problems can be avoided by regular cleaning of the reagent area. In this way, large but infrequent discharges of reagent-rich wastes to the

tailings area are avoided. Spills of liquid or solid reagents should be collected, if possible, and disposed of in an area where the possibility of contamination of the recycle water is low. If possible, the wash water from the reagent storage area should be directed to an engineered pond where the contaminated waste could be held for a period of time in order to permit the decomposition of the reagents that will break down in a natural environment. The overflow from such a pond could be directed to the tailings area. If the pond was large enough (perhaps 1 acre), it would act to equalize waste flows from the reagent area and would prevent accidental reagent spills from adversely influencing the recycle water.

(2) Mill reagent concentrations found in mine water are generally less than those found in mill water. Although mill reagents are seldom used underground in a mine, they can appear in the mine water simply because mill water (containing the reagents) is used to repulp and convey coarse tailings underground for use as backfill. Where backfill is not used, the mine water can be essentially free of common mill reagents (oil, etc., may still be a problem).

Therefore, under some circumstances, mine water can take the place of fresh make-up water in the mill where make-up water is required and still not affect the quality of the recycle stream to any great extent.

THE CHEMICAL OXYGEN DEMAND (COD) AND BIOCHEMICAL OXYGEN DEMAND (BOD) OF MINE-MILL REAGENTS

Chemical oxygen demand and biochemical oxygen demand determinations were carried out on a number of commercial (Cyanamid) mine-mill reagents. Concerning the results (tabulated at the end of this section) of the determinations, the following important facts should be noted:

- (1) The results listed are expressed as milligrams of oxygen demand (BOD or COD) per kilogram of commercial product.
- (2) The BOD and COD values listed may or may not correspond to the theoretical values that can be derived for each formulation. Very few, if any, of the commercial reagents listed consist of a single, 100 percent pure compound and, in most cases, more than one specific identifiable compound is present in the formulation.
- (3) Only very rarely will any specific commercial reagent exist in the effluent from a typical tailings area in concentrations greater than 5 parts per million. Only occasionally will any specific commercial reagent exist in the effluent from a typical tailings area in concentrations greater than 3 parts per million. The most common concentration of a commercial product in a typical tailings area effluent appears to be 2 parts per million or less.

<u>Name of Product</u>	<u>Milligrams per kilogram</u>	
	<u>BOD</u>	<u>COD</u>
Aero Xanthate 301	20,000	1,900,000
Aero Xanthate 303	24,000	1,040,000
Aero Xanthate 317	68,000	1,900,000
Aero Xanthate 325	44,000	1,320,000
Aero Xanthate 343	10,000	1,410,000
Aero Xanthate 350	4,000	1,600,000
Aerofroth 65 Frother	540,000	2,900,000
Aerofroth 71 Frother	880,000	2,300,000
Aerofroth 53 Frother	990,000	1,900,000
Aerofroth 61 Frother	160,000	1,400,000
Aerofroth 73 Frother	240,000	1,500,000
Aerofroth 77 Frother	84,000	1,500,000
Aero Promoter 404	*	1,100,000
Aero Promoter 407	*	1,300,000
Aero Promoter 412	*	1,300,000
Aero Thiocarbanilide 130	76,000	4,900,000
Aero Promoter 3302	26,000	2,100,000
Aero Promoter 3461	*	2,100,000
Aero Promoter 3477	*	1,010,000
Aero Promoter 3501	*	900,000
Aero Promoter 710	560,000	1,060,000
Aero Promoter 801	**	900,000
Aero Promoter 825	*	2,600,000
Aero Promoter 830	92,000	580,000
Aero Promoter 845	*	23,000
Aeromine 3037	76,000	2,000,000
Aerofloat 15 Promoter	12,000	2,200,000
Aerofloat 25 Promoter	**	2,900,000
Aerofloat 31 Promoter	*	2,300,000
Aerofloat 33 Promoter	**	1,600,000
Aerofloat 242 Promoter	220,000	1,800,000
Sodium Aerofloat Promoter	*	1,180,000
Aerofloat 208 Promoter	*	1,030,000
Aerofloat 211 Promoter	*	900,000
Aerofloat 238 Promoter	*	1,080,000
Reagent S-3543	76,000	2,200,000
Aerosol C-61	*	1,900,000
Aerosol GPG	136,000	1,210,000
Aero Depressant 610	140,000	900,000
Aero Depressant 633	600,000	1,100,000

<u>Name of Product</u>	<u>Milligrams per kilogram</u>	
	<u>BOD</u>	<u>COD</u>
Cyquest 3223 Antiprecipitant	*	40,000
Aerofloc 550 Reagent	26,000	2,500,000
Superfloc 16 Flocculant	8,000	900,000
Superfloc 127 Flocculant	24,000	200,000
Superfloc 202 Flocculant	38,000	1,000,000
Superfloc 214 Flocculant	70,000	500,000
Superfloc 310 Flocculant	*	9,200

* No reliable results could be obtained. Bacteriacidal effects due to reagent suspected (OWRC). Cyanamid comments:

"These reagents are either not biodegradable due to their chemical composition, toxic to the seed organisms, or may have a lag period and would require a period of acclimatization."

** Oily layer interference. .

NOTE: The toxicities of Cyquest 3223 Antiprecipitant, Aerosol C-61 and Aerosol GPG are given below:

(i) Cyquest 3223 Antiprecipitant

Chemistry: An acrylic polymer

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1,000 to 10,000 ppm ^w /v	relatively non-toxic

(ii) Aerosol C-61

Chemistry: Cationic; mixture of the octadecyl amine and octadecyl guanidine salts of octadecyl carbamic acid reacted with ethylene oxide.

Toxicity (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	1 to 10 ppm ∇ /v	moderate toxicity

(iii) Aerosol GPG

Chemistry: Anionic; Di (2-ethylhexyl) sodium
sulfosuccinate

Toxicity: (OWRC Lab. Value):

<u>Organism</u>	<u>Toxicity Range</u>	<u>Toxicity</u>
P. Promelas	10 to 100 ppm ∇ /v	moderate toxicity

TAILINGS AREA DESIGN AND ITS RELATIONSHIP TO THE TOXICITY AND BIODEGRADABILITY OF MINE-MILL REAGENTS

The design of a tailings area, especially a tailings area that is to be incorporated into a wastewater recycle scheme, should not be finalized until the following factors have been taken into consideration:

- (1) Many important mine-mill reagents are organic compounds. In a favourable environment, most of these compounds will exhibit a degree of biodegradability.
- (2) Residual concentrations of mine-mill reagents have been identified in the effluents from mining operations that work sulphide ores. Xanthate residuals of 0.2 to 1.2 mg/litre and dithiophosphate residuals in the range of 0.3 to 2.7 mg/litre have been noted. In one case, isopropyl ethylthionocarbamate was detected in an effluent at a concentration of 1.8 mg/litre.
- (3) In general, the constituents of frothers are volatile substances. Accordingly, a substantial quantity of the frothers added in flotation operations is volatilized so that re-use of flotation tailing waters does not necessarily reduce proportionately the requirement for frothers.

Unwanted quantities of a particular frother appearing in a recycle stream (from a tailings area, etc.) can

probably be reduced or eliminated by:

- (a) increasing the retention time of the frother-containing wastes before recycle to the mill; or
- (b) applying a degree of mechanical aeration, etc., to the frother-containing waste; or
- (c) selecting another frother with superior breakdown properties for use in the mill.

If the breakdown properties of a particular frother are known, then the actual waste retention time in the tailings area serving the operation can probably be increased to effect substantially a complete breakdown (or loss) of the frother or decreased to prevent frother loss or breakdown (if this is desired).

(4) The xanthates are among the most toxic reagents that find common use in a sulphide mill circuit. They are, however, quite unstable in aqueous solution and break down into relatively innocuous substances (see section concerning xanthates). At temperatures above 30°C and at low (xanthate) concentrations (such as found in a tailings decant), and exposure to acidic conditions, decomposition of xanthates is extremely rapid. Therefore, it appears that residual xanthate

concentrations can be reduced by increasing waste retention times and by decreasing solution pH values.

(5) The recirculation of mine-mill wastewaters is now becoming commonplace in the Province of Ontario. Wastewater re-use is a standard recommendation of the Ontario Ministry of the Environment. Therefore, a tailings area should be designed with wastewater recirculation in mind. In essence, this means that the tailings area decant should be directed to a secondary (or downstream) area where chemical waste treatment and final solids removal can take place. When this has been accomplished, the clarified waste can be used for recycle purposes.

It is important to note that it is not wise to recycle wastewater (especially at a small mining operation) from the decant pond itself. The reason for this is that the presence of rock slimes (very finely divided rock particles) can seriously inhibit mill processes such as differential flotation and ion exchange with resultant losses in metallurgical efficiency. If necessary, aerators, etc., can be installed in the secondary area in order to enhance the breakdown or removal of residual quantities of undesirable reagents.

MINE-MILL REAGENT LOSSES

A mine-mill circuit is said to 'consume' the reagents that are fed to it. That is, the reagents undergo physical and/or chemical changes during the milling and subsequent conventional waste treatment processes and, as such, in most cases, become unrecognizable and unrecoverable in their original form.

Simply speaking, the following factors determine whether or not a particular reagent or any quantity of it will escape a mining property in more or less its original form:

- (i) the physical and/or chemical properties of the reagent itself;
- (ii) the type and size of the milling circuit;
- (iii) the type and size of the tailings impoundment area; and
- (iv) the composition of the ore and country rock.

It is difficult to predict the quantity of a particular mine-mill reagent that will be lost to the immediate aqueous environment (the receiving stream) based on mill addition rates of that specific reagent. However, when enough detailed information from a number of mining properties is available, the prediction can be made with a

fair degree of accuracy. For instance, in the Province of Ontario, it has been found that cyanide losses from active mine-mill operations to receiving streams approximate 0.02 to 0.5 percent of total cyanide mill additions. In the near future, it will be possible to make similar but more accurate predictions concerning materials such as xanthates and dithiophosphates.

LUBRICANTS

Mining and milling are very mechanized operations. Most mine-mill equipment requires lubrication. It is therefore not unreasonable to expect trace quantities of the various lubricants in use in mine-mill circuits to appear in mine-mill effluents.

The lubricants that are being used by the mining industry are generally based on various grades of mineral and non-mineral oils. The use of 'additives' in these oils to achieve specific desired effects is an almost universal practice.

The various types of additives presently in use are as follows:

(i) Viscosity Index Improvers

Used to improve viscosity-temperature relationships of the lubricant to minimize viscosity change over the operating temperature range. These are usually polymeric materials such as polyisobutylene or polymethacrylate. They are susceptible to shear breakdown to products of lower molecular weight.

(ii) Antifoam Agents

Used to prevent foaming and to accelerate foam

breakdown. Silicone fluids in concentrations of from 0.01 to 0.001% or less are most commonly used for this purpose.

(iii) Oxidation Inhibitors

Used to delay or inhibit oxidative breakdown of the oil and formation of sludge, lacquers, corrosive by-products and other undesirable products of oxidation. These may act as inhibitors by competing with the hydrocarbon for oxidation, as peroxide decomposers which destroy the peroxide formed due to oil oxidation and preventing further oxidation, and as retardants which upon oxidation form inhibitors.

Phenols, amines and sulphur compounds containing phosphorous, sulphur and/or nitrogen and combinations of the above are frequently used.

(iv) Rust Inhibitors

Used to prevent the formation of rust on ferrous metals in the presence of corrosive by-products of hydrolysis and oxidation as well as that caused by presence of water.

Rust inhibitors are generally polar, surface active compounds which tend to cover the iron or steel with a water repellant film. Typical products are metal sulphonates, fatty amines, long chain fatty alcohols, acids and esters and reducing agents

such as sodium nitrite.

(v) Corrosion Inhibitors

Used to prevent corrosion of various bearing metals and will vary with the metal combination to be protected. Metallo dialkyl and diaryl dithiophosphate esters in concentrations of 0.2 to 3 percent are frequently used for this purpose.

(vi) Friction Modifiers

Used to reduce kinetic and static co-efficient of friction. A variety of chemical compounds have been used for this purpose.

(vii) Detergent-Dispersants.

Used to keep sludge and materials which might deposit as varnish in colloidal suspension and keep metal surfaces clean. These materials are not normally used, as such, in industrial gear oil formulations; however, corrosion inhibitors present may act as detergent-dispersants.

(viii) Metal Deactivators

Used primarily with copper or its alloy, bronze, to form strongly bonded chelate compounds which are inactive as catalysts for oil oxidation and may react with the metal to

form a passive surface. These are usually highly specific organic compounds such as NN-disalicylidene 1, 2 propylene diamine normally used at concentrations of from 5 to 10 ppm.

(ix) Pour Point Depressants

Used to reduce pour point or channel point of wax-containing base oils so they will flow freely at lower ambient temperatures. They act by altering the crystal structure of the wax and permit movement of the oil. They are usually methacrylate polymers or wax condensation products of naphthalene or phenol and are used in concentrations of from 0.5 to 5 percent.

(x) Tackiness Agents

Used to increase the adhesiveness of gear oils. High molecular weight hydrocarbon polymers, naturally occurring petroleum resins and natural crepe rubber are products frequently used for this purpose. As little as 0.01 percent of this type compound is effective.

(xi) Anti-Wear Agents

Used as anti-weld agents and wear preventatives in steel on steel applications. They are believed to act as chemical polishing agents generally at a lower temperature

than anti-weld films formed by EP agents although very similar. Typical of anti-wear additives are tricresyl phosphate and zinc dialkyl dithiophosphate.

(xii) Extreme Pressure Additives

Used to prevent welding and scoring of metal surfaces by forming easily sheared films resulting from the chemical reaction of chlorine, sulphur and phosphorous compounds or formation of low melting point eutectic alloys on the surface of the gear. EP gear oils are frequently classified according to type, i.e., (1) non-corrosive sulphurized fatty oil, (2) non-corrosive lead soap inactive sulphur with or without phosphorus and polar compounds, (3).corrosive lead soap active sulphur, (4) non-corrosive chlorine, sulphur and phosphorus (5) non-corrosive sulphur, chlorine, lead soap with or without polar agent, (6) sulphur, chlorine, phosphorus , zinc and (7) sulphur- phosphorus combinations.

Very little work has been done to delineate the environmental effects of specific lubricants being used by the mining industry. However, in general, adequate toxicity information concerning individual substances (additives) and individual oils is available from diverse sources. The

relatively low volume and controlled use of lubricants tends to indicate that, under conditions of normal use, severe environmental problems would not be expected.

EXPLOSIVES

The mining industry is one of the few industries that uses explosives on a routine basis. In fact, without the general availability of explosives, most Canadian mining operations would cease to exist.

Commercial explosives are chemical substances. With few exceptions, these solid or liquid substances are materials that are capable of rapid and violent decomposition into large volumes of gas. Decomposition of a "high" explosive such as dynamite takes place with extreme rapidity while in the case of a "low" explosive such as black blasting powder, it takes place much more slowly.

When properly initiated, explosives are converted into gases at high temperature and tremendously increased volume which causes pressure to be exerted on the confining material. The effectiveness of explosives in blasting is due to the speed with which the gas pressure is developed. The energy released acts equally in all directions but naturally tends to escape via the path of least resistance.

Does the use of explosives at a mining operation have any effect on the chemical characteristics of the mine

water? Little or no work has been done in this regard but one would expect at least minor changes in mine water chemistry as a result of the use of explosives.

Consider, for instance, the chemical characteristics of the types of explosives that find common use:

(a) Straight Nitroglycerin Dynamite

The explosive base of straight nitroglycerin dynamite is liquid nitroglycerin. This is absorbed in a mixture of various carbonaceous materials such as wood pulp and ground meal. Another common ingredient is sodium nitrate which is used principally to supply oxygen for the complete combustion of the carbonaceous materials.

(b) Ammonia Dynamites

Ammonia dynamites make use of ammonium nitrate as a substitute for a portion of the liquid nitroglycerin.

(c) Gelatin Dynamites

Gelatin dynamites have as a base a water resistant "gel" made by dissolving nitrocotton in nitroglycerin. The gel may vary from a thick, viscous liquid to a tough rubber-like substance. It is insoluble in water and tends to water-proof other ingredients with which it is mixed, at the same

time binding them together and rendering the mass cohesive and plastic in nature.

(d) Semi-Gelatin Dynamites

In the semi-gelatin dynamites, some of the economy of ammonia dynamites and the water resistance and cohesiveness of gelatins have been combined.

(e) Permitted Explosives

A permitted explosive is one which has successfully passed certain British or U.S.A. standard tests and, as a result, has been classed as safe for blasting in gassy or dusty mines provided that it is used in a specified or "permitted" manner. The essential difference in composition between permitted explosives and others is that they are designed to produce flame of the least volume, lowest temperature, and shortest duration possible. Certain salts are incorporated in their make-up which have a cooling or quenching effect on the flame.

(f) Blasting Agents

Blasting agents consist largely of ammonium nitrate and differ radically in appearance and properties from high explosives. Their outstanding characteristic is their com-

parative safety in handling and use due to their relatively low sensitivity to shock, friction and impact. One of the most popular blasting agents (used, in particular, at open pit operations) is a simple mixture of fuel oil and prilled ammonium nitrate. This agent is referred to as AN/FO. The most common AN/FO mixture consists of (by weight) 6% No. 2 diesel oil and 92% prilled ammonium nitrate.

Many substances not mentioned are used as or are associated with explosives. These substances include metal powders, trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN) and ethylene glycol dinitrate.

The gases resulting from the detonation of commercial explosives are principally carbon dioxide, nitrogen and water vapour. The principal 'toxic' or 'poisonous' gases are carbon monoxide and oxides of nitrogen.

It is reasonable to assume that the detonation of most explosive charges is not 100 percent efficient. As a result, it is reasonable to assume that very small but nonetheless real quantities of unburned or partially burned explosive substances remain with the broken rock after a detonation. If the broken rock is wetted (as it almost

invariably is), any water soluble component (for example, ammonium nitrate) of the residual explosive will tend to go into solution. Hence, changes in mine water chemistry can be expected. However, in general, these changes will be slight. For instance, the nutrient (nitrogen, etc.) load carried by the mine water will probably be increased slightly by the use of explosives in mining operations.

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